PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
Volume 14 October 15, 1928 Number 10

IS IT POSSIBLE TO TEST BY A DIRECT EXPERIMENT THE HYPOTHESIS OF THE SPINNING ELECTRON?

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Read before the Academy April 23, 1928

1. In order to interpret the multiplet structure of the line spectra, it was supposed[1] that the electron is not merely an electric charge, but that it has a spin angular momentum $\left(\frac{1}{2}\,\frac{h}{2\pi}\right)$ and a magnetic moment (equal to one Bohr magneton). When there is a magnetic field acting upon the electron, the axis of rotation must lie in the direction of the field. This gives two different orientations, according to the magnetic moment having the same direction as the field, or the opposite direction. For each quantized orbit of the electron, we shall get two different energy levels, corresponding to these two different orientations; this is the explanation of the well-known sodium doublet, for instance.

It would be very desirable to test this hypothesis by a direct experimental method, in order to be sure that this "duplexity" is really a fundamental property of the electron itself, and not a special property of atomic structures. Unfortunately, it happens that in most experimental cases, the effect of the magnetic moment of the electron is so small that it is quite impossible to observe it.

2. I suggested[2] one year ago a special plan by which it seemed possible to get a measurable result. The general idea was the following: Suppose a beam of electrons is coming into a weak magnetic field. The trajectories will turn around the direction of the magnetic field (say, the OZ axis) and if the field is constant the electrons describe spirals; the velocity v_z along the Z axis remains constant; the radius of the cylinder, upon which the spiral is traced, is equal to $\frac{m\,v_n}{e\,H}$, H being the magnetic field, and v_n the component of the velocity of the electrons, in a plane perpendicular to H.

I supposed such a beam of electrons, coming at A in a magnetic field, under almost normal incidence (v_z very small) and beginning to describe

their spirals; the velocity v_z along the direction of the field was supposed to remain constant, even in the case of a non-uniform magnetic field. So the electrons would follow the magnetic line of force (Fig. 2) until they reached the magnetic pole; the electrons could be collected by an electrode B, at the magnetic pole, and the current measured in any convenient way.

Fig. 1

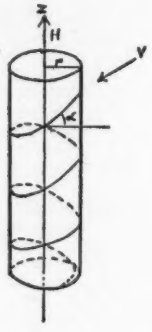


Fig. 2.

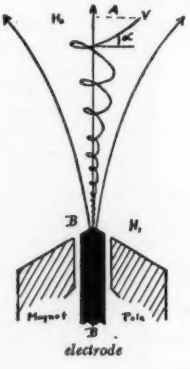
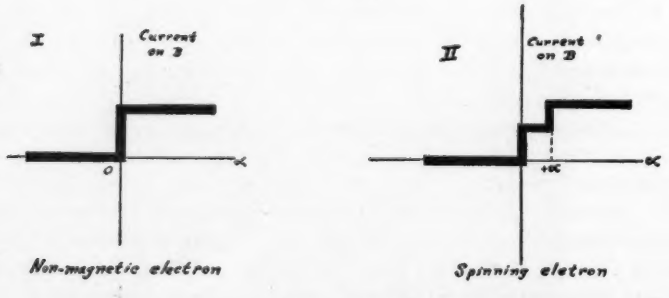


Fig. 3.



3. If now we suppose that the electron has a magnetic moment μ, we must pay attention to the magnetic force $f_z = \mu \dfrac{\partial H}{\partial z}$ acting upon the magnetic electron. When the electron moves from A (magnetic field H_0) to B, where the field is H_1, the work done by the magnetic force is

$$\int_A^B f_z \, dz = \int_A^B \mu \frac{\partial H}{\partial z} \, dz = \mu \, (H_1 - H_0). \qquad (1)$$

Thus the velocity v_z of the electron along the Z axis will no more be constant, but

$$\frac{1}{2} m (v_{z1}^2 - v_{z0}^2) = \mu (H_1 - H_0).$$

Half of the electrons have their magnetic moments in the positive direction and will therefore be attracted; the other half have a negative magnetic moment, and will be repelled. If $H_1 - H_0$ is great enough, they will be checked before reaching the magnetic pole and the electrode B. This will occur if $v_{z1} = 0$

$$H_1 - H_0 = \frac{m}{2|\mu|} v_{z0}^2 = \frac{mv^2}{2|\mu|} \sin^2 \alpha = \frac{eV}{|\mu|} \sin^2 \alpha. \qquad (2)$$

α is the angle between the initial velocity v of the electrons, and the $x\ o\ y$ plane; V is the accelerating potential. Here we must see the orders of magnitude:

$$e = 4.774 \quad 10^{-10} \quad E\,S\,c\,g\,s$$
$$V = 1 \text{ volt} = \frac{1}{300} \quad E\,S\,c\,g\,s$$
$$N = 6.06\ 10^{23} \qquad \text{Avogadro's number}$$
$$\mu = \frac{5584}{N} = 0.9215 \quad 10^{-20}.$$

With $\sin \alpha = 0.01$ we get $H_1 - H_0 = 17{,}300$ gauss. The experiment would then be made this way: First, start with electrons entering the field under an angle α which is not too small. All these electrons would reach the electrode B; then we would decrease progressively the angle α and plot the current received on the electrode B. If the electrons had no magnetic moment, the current would fall suddenly when α [Fig. 3, Curve I] becomes zero. If the electrons have a magnetic moment μ we must observe first a decrease of the current to one-half its initial value, when α reaches the critical angle (2); and the current would fall down to zero for the angle 0. (Fig. 3, Curve II.)

4. I had the pleasure of discussing the matter some months ago with Dr. A. W. Hull, who made an important criticism of my deduction. He pointed out that the assumption of par. 2 is not true. When the electron moves in a non-uniform field, the component of its velocity along the direction of the field does not remain constant. Consider the trajectory as drawn in figure 2 or 4; we suppose that the field is symmetrical with respect to the Z axis. When turning around the Z axis, the electron is in a region (say P) where the field is not parallel to the Z axis; thus the force, being perpendicular to the field, has a component along Z, and the velocity v_z cannot remain constant. Dr. Hull worked out some approximate cal-

culations upon this perturbation, and I will give here a more precise statement of the problem.

A non-uniform field, symmetrical around the Z axis, may be obtained from the following potential vector

$$A_x = \frac{1}{2}\varphi(z)\, y \qquad A_y = -\frac{1}{2}\varphi(z)x \qquad A_z = 0 \tag{3}$$

Fig. 4.

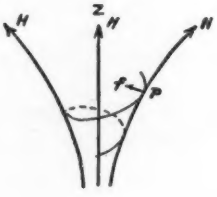


Fig. 5.

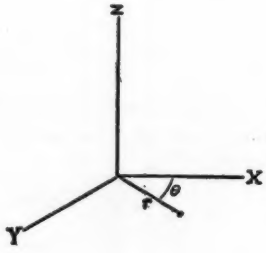


Fig. 7.

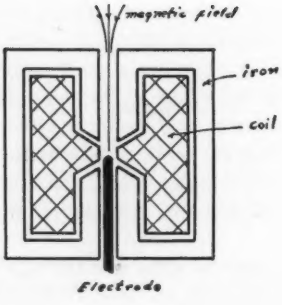
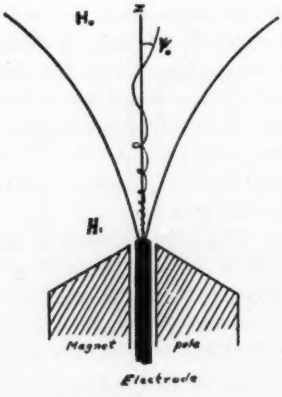


Fig. 6.



$\varphi(z)$ being any function of Z; the components of the field are

$$H_x = \frac{x}{2}\frac{\partial\varphi}{\partial z} \qquad H_y = \frac{y}{2}\frac{\partial\varphi}{\partial z} \qquad H_z = -\varphi(z). \tag{4}$$

The motion of the electrons may be deduced from the Lagrange function

$$L = \frac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + e (\dot{x}A_x + \dot{y}A_y + \dot{z}A_z)$$

or, using polar coördinates r and θ in the xy plane

$$L = \frac{m}{2}\left[\dot{r}^2 + r^2\dot{\theta}^2 + \dot{z}^2\right] - \frac{e}{2}\varphi(z) r^2\dot{\theta}. \tag{5}$$

The term involving the vector potential is $\frac{e}{2}\varphi(\dot{x}y - \dot{y}x)$ and reduces to the form (5). The momenta corresponding to r, θ, z are

$$p_r = \frac{\partial L}{\partial \dot{r}} = m\dot{r} \qquad p_z = \frac{\partial L}{\partial \dot{z}} = m\dot{z} \qquad p_\theta = \frac{\partial L}{\partial \dot{\theta}} = mr^2\dot{\theta} - \frac{e}{2}\varphi r^2 \tag{6}$$

and the equations of motion take the following form

$$\dot{p}_r = \frac{\partial L}{\partial r} = mr\dot{\theta}^2 - e\varphi r\dot{\theta} \tag{7.1}$$

$$\dot{p}_z = \frac{\partial L}{\partial z} = -\frac{e}{2}\frac{\partial \varphi}{\partial z} r^2\dot{\theta} \tag{7.2}$$

$$\dot{p}_\theta = \frac{\partial L}{\partial \theta} = 0 \qquad p_\theta = C^{te} \tag{7.3}$$

The expression p_θ remains constant, and is therefore an integral of the motion. We can easily find a second integral, which is the total kinetic energy of the electron; the magnetic field exerts a force normal to the velocity and does no work; this may be found directly from our equations

$$E = \frac{1}{2} m\left[\dot{z}^2 + \dot{r}^2 + r^2\dot{\theta}^2\right] = \frac{1}{2} m\left[\dot{z}^2 + \dot{r}^2\right] + \frac{1}{2m}\left[\frac{p_\theta}{r} + \frac{e\varphi r}{2}\right]^2. \tag{8}$$

The second expression is obtained by replacing $\dot{\theta}$ by its value taken from equations (6) and (7.3)

$$\dot{\theta} = \frac{p_\theta}{mr^2} + \frac{e\varphi}{2m}.$$

5. The general problem being rather intricate, we shall make an approximation and suppose that the rate of change of the magnetic field along the Z axis is very small; for each value of Z we assume that the electron is performing its motion almost as in a constant field.

Furthermore, we shall study the motion of an electron describing a spiral around the Z axis. That is, we suppose the projection of the motion on the xy plane to be centered on 0.

As the electron will always describe a spiral around one of the magnetic lines of force, this second hypothesis does not introduce any special restriction.[3]

From equation (7.1) we see that, to a first approximation, the projection of the motion of the electron on the xy plane is a circle

$$\dot{p}_r = m\ddot{r} = 0 \qquad \dot{\theta} = \frac{e\varphi}{m} \tag{9}$$

If φ is not a constant, but varies slowly as a function of z, the angular velocity $\dot{\theta}$ will be very nearly equal to $\frac{e\varphi}{m}$ and $\ddot{r}$ will not be zero, but very small; we must satisfy the condition (7.3)

$$p_\theta = mr^2\dot{\theta} - \frac{e\varphi}{2} r^2 \approx \frac{e\varphi}{2} r^2 = C''. \tag{10}$$

Hence,

$$r^2 = \frac{2p_\theta}{e\varphi}. \tag{11}$$

If we call ψ the angle of the velocity v of the electrons with the Z direction

$$\dot{z} = v\cos\psi \qquad r\dot{\theta} = v\sin\psi$$

we can write the condition (10) in the following form (using Eq. 9)

$$p_\theta = \frac{e\varphi}{2} r^2 = r^2\dot{\theta}^2 \frac{m^2}{2e\varphi} = \frac{m^2v^2}{2e\varphi}\sin^2\psi \tag{12}$$

v is a constant on account of the conservation of the kinetic energy, and we get the very simple result

$$\frac{\sin^2\psi}{\varphi} = C' = \frac{\sin^2\psi_0}{\varphi_0}. \tag{13}$$

6. Now we can return to our experimental arrangement. Suppose our electrons to enter the field in a region where the magnetic field $H_0 = -\varphi_0$ is very small; they will be able to penetrate into greater fields if the angle ψ_0 is small, but when the field increases, ψ increases, and the electrons will stop when ψ becomes equal to $\frac{\pi}{2}$; this corresponds to a field

$$\varphi = \frac{\varphi_0}{\sin^2\psi_0}. \tag{14}$$

Such will be the result for a non-magnetic electron. For a spinning electron, we must take account of the work done by the magnetic force acting upon the electron, as calculated in paragraph 3.

If the sign of the magnetic moment of the electron is right, the electron when coming into the field φ defined by equation (14) will still have a small velocity v_z along the Z axis; this velocity is directly connected with the work $\mu(\varphi - \varphi_0)$ done by the magnetic forces[4]

$$\frac{1}{2} m v_z^2 = \mu (\varphi - \varphi_0). \tag{15}$$

The angle ψ, instead of being $\frac{\pi}{2}$, will have a slightly different value

$$\sin^2 \psi = 1 - \frac{v_z^2}{v^2} = 1 - \frac{2\mu}{mv^2} (\varphi - \varphi_0).$$

Hence, such electrons would be able to travel somewhat farther, until they reach a greater field

$$\varphi_1 = \frac{\varphi}{\sin^2 \psi} = \varphi \left[1 + \frac{2\mu}{mv^2} (\varphi - \varphi_0) \right]. \tag{16}$$

Electrons having their magnetic moment in the wrong direction could only reach the field

$$\varphi_2 = \varphi \left[1 - \frac{2\mu}{mv^2} (\varphi - \varphi_0) \right].$$

Thus, the difference between the magnetic stopping fields would be

$$\varphi_1 - \varphi_2 = \Delta\varphi = \frac{4\mu}{mv^2} \varphi(\varphi - \varphi_0) \approx \frac{4\mu\varphi^2}{mv^2} = \frac{2\mu\varphi^2}{eV} \tag{17}$$

since $\varphi - \varphi_0$ is very nearly equal to φ, and V is the accelerating potential of our electrons.

Using formula (13) we see that this would correspond, for the initial angle ψ_0 of the electrons entering the field, to a variation

$$\Delta (\sin \psi_0) = -\frac{1}{2} \sqrt{\frac{\varphi_0}{\varphi}} \frac{\Delta\varphi}{\varphi} = -\frac{2\mu}{mv^2} (\varphi - \varphi_0) \sqrt{\frac{\varphi_0}{\varphi}} \approx -\frac{2\mu}{mv^2} \sqrt{\varphi\varphi_0} \tag{18}$$

with the approximation that $\varphi - \varphi_0$ is very nearly equal to φ.

7. Numerical calculations prove that the angles corresponding to the formula (18) are extremely small. Take the numerical data of paragraph (3) and electrons accelerated by only one volt; in order to be able to define their direction by convenient screens, we must suppose that they start in a very weak magnetic field, say $-\varphi_0 = 1$ gauss; supposing $-\varphi$ to be equal to 30,000 gauss, we get

$$\sin \psi_0 = \sqrt{\frac{\varphi}{\varphi_0}} = 0.58\ 10^{-2}$$

$$\Delta \sin \psi_0 = 10^{-6}.$$

The difference $\Delta\varphi$ between the stopping magnetic field would be

$$\Delta\varphi = 10.4 \text{ gauss.}$$

Theoretically, when varying the angle of the incident beam, or the magnetic field, in the neighborhood of the value corresponding to the stopping field, we should observe a curve similar to curve II, figure 3, with a current first falling down to half its maximum value and afterward becoming zero. Unfortunately, the orders of magnitude seem to be rather discouraging; I had made some calculations upon the electromagnet, and found that a shape like the one drawn in figure 6 would be the best one. The coil is coming very near the top of the magnet pole, where we place our electrode collecting the electrons; the line of force which comes through the hole of the opposite magnet pole satisfies the conditions that we need in our experiment; it comes from far away, where the magnetic field is very weak, and the electrons following it would fall in a very strong field when coming near the top of the other pole.

As a conclusion, we must say that the experiment seems to be a very difficult one; the conditions would perhaps be better if we add an electric field along the Z axis (that is, along the direction of the magnetic field). This electric field could give an acceleration in the Z direction and compensate the retarding magnetic force calculated in paragraphs 4 and 5; thus we could work with electrons moving with an almost constant velocity along the magnetic field, as supposed in paragraphs 2 and 3, where the conditions seemed rather better.

[1] A. L. Parson, *Smiths. Misc. Coll.*, p. 65 (1915). A. H. Compton, *Journ. Franklin Inst.*, p. 145 (1921). S. Goudsmit and G. E. Uhlenbeck, *Naturwiss.*, **13** (1925), p. 953; *Nature*, **117** (1926), p. 264; *Physica*, **6** (1926), p. 273. F. R. Bichowski and H. C. Urey, *Proc. Nat. Acad. Sci.*, **12** (1926), p. 80. L. H. Thomas, *Nature*, **117** (1926), p. 514; *Phil. Mag.*, **3** (1927), p. 1; and many other new works in connection with the new mechanics.

[2] L. Brillouin, *Compt. rendus, Acad. Sci. Paris*, **184** (1927), p. 82.

[3] If we neglect the effect of the variation of φ the solution of the equations (7.1) and (7.3) is a spiral drawn on a circular cylinder; we suppose this cylinder to have the oz axis as axis of symmetry.

[4] The calculation may be given here with more details; for non-magnetic electrons we should have, on account of (13),

$$2\beta \frac{d\beta}{dt} = \frac{\beta_0^2}{\varphi_0} \frac{\partial \varphi}{\partial z} v_z \text{ with } \beta^2 = \sin^2 \psi = 1 - \frac{v_z^2}{v^2}.$$

For our magnetic electrons, we have the magnetic force $\mu \dfrac{\partial \varphi}{\partial z}$ which tends to increase the

v_z component; this force alone would give $\dot{v}_z = \frac{\mu}{m}\frac{\partial \varphi}{\partial z}$. On account of the relation $\beta\dot{\beta} = -\frac{v_z \dot{v}_z}{v^2}$, this adds a term $-\frac{\mu}{mv^2}\frac{\partial \varphi}{\partial z}\frac{v_z}{\beta}$ to the variation of β; so we must write

$$\frac{d\beta}{dt} = \frac{\beta_0^2}{2\beta\varphi_0}\frac{\partial \varphi}{\partial z}v_z - \frac{\mu}{mv^2}\frac{\partial \varphi}{\partial z}\frac{v_z}{\beta} \quad \text{or} \quad \frac{d\beta}{d_z} = \frac{1}{v_z}\frac{d\beta}{dt} = \frac{1}{\beta}\frac{\partial \varphi}{\partial z}\left[\frac{\beta_0^2}{2\varphi_0} - \frac{\mu}{mv^2}\right].$$

The integration is immediate and yields $\beta^2 = \beta_0^2\frac{\varphi}{\varphi_0} - \frac{2\mu}{mv^2}(\varphi - \varphi_0)$. The stopping field is obtained for $\beta = 1$, and, on account of the fact that the term in μ is very small, we can write

$$\varphi_1 = \frac{\varphi_0}{\beta_0^2}\left[1 + \frac{2\mu}{mv^2}(\varphi - \varphi_0)\right] = \varphi\left[1 + \frac{2\mu}{mv^2}(\varphi - \varphi_0)\right].$$

In the integration, we have treated mv^2 as a constant, an approximation actually justified if we take account of the very small magnitude of the magnetic forces.

ON THE DISTRIBUTION LAW IN LOCALLY RAPIDLY FLUCTUATING FIELDS WHICH ARE STEADY WHEN AVERAGED OVER A SUFFICIENT TIME INTERVAL

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Communicated August 27, 1928

Thomas[1] and later Fermi[2] have attempted to determine the time average electrical potential around the nucleus of a heavy atom. They treat the electrons as if they formed an ideal degenerate Fermi gas which becomes statistically distributed in the steady field due to the nucleus plus the locally rapidly fluctuating field due to the electrons themselves. This method is apparently fully justified and it is hard to see, at first, why the numerical solutions given by the above writers turn out to be so roughly approximate, especially for heavy atoms with many electrons. The following investigation purports to show that the roughness of the method is due to the unjustified, except for approximation purposes, use of the statistical distribution law of an ideal gas in a *steady* field in the case where the field is steady only when averaged over a sufficiently long time interval and is locally fluctuating. It is shown that if there is any correlation between the local fluctuations in density and local fluctuations in the field that additional time-average forces arise which are derivable from a potential. This "correlation potential" must be introduced in the distribution law in order that the above-mentioned method should be precise.

Consider a small element of volume Δv in a locally fluctuating field of force, which is so small that the fraction of the time that more than one particle of an ideal gas acted upon by this field is in Δv is negligible. Let $G_k(t)$ $(k = 1,2,3)$ be the component of the instantaneous forces per unit mass acting on Δv. Let $\rho(t)$ be the instantaneous density in Δv. $\rho(t)$ is on the whole equal to $m/\Delta v$ or 0, where m is the mass of a particle. Then the instantaneous component of force on the element Δv is $G_k(t)$ $\rho(t)\Delta v$.

Let T be a sufficiently long time interval so that the distribution of the gas and the field are steady when averaged over the time T. The average forces on gas in Δv are then $(1/T) \int_0^T G_k(t)\rho(t)\Delta v dt$. For time average momentum equilibrium in the element Δv we have

$$\frac{\partial p}{\partial x_k} \Delta v = \frac{1}{T} \int_0^T G_k(t)\rho(t)\Delta v dt \tag{1}$$

where p is the pressure which is already a time-averaged quantity.

Let $g_k = (1/T)\int_0^T G_k(t)dt$ be the average value of $G_k(t)$ and let $r = (1/T)\int_0^T \rho(t)dt$ be the average value of $\rho(t)$. Let $h_k(t) = G_k(t)\, g - g_k$ and $s(t) = \rho(t) - r$ be the corresponding instantaneous deviations from the average values. Then (1) becomes

$$\frac{\partial p}{\partial x_k} = \frac{1}{T} \int_0^T [h_k(t)s(t) + h_k(t)r + g_k s(t) + g_k r]dt,$$

that is,

$$\frac{\partial p}{\partial x_k} = g_k r + \frac{1}{T} \int_0^T h_k(t)s(t)dt. \tag{2}$$

The second term on the right will only vanish when there is no correlation between the deviations from the average of density and the deviations from average of the external force per unit mass. When it does vanish then

$$\frac{\partial p}{\partial x_k} = g_k r. \tag{3}$$

If the temperature is uniform the law of statistics enables one to determine p as a function $p(r)$ of r so that, as in the classical distribution law

$$g_k = \frac{\partial}{\partial x_k} \int \frac{dp}{r} = -\frac{\partial V}{\partial x_k}, \; (k = 1,2,3) \tag{4}$$

which gives

$$V = -\int \frac{dp}{r} = \text{const.} \tag{5}$$

which on evaluating the integral and solving for r gives the distribution law sought for.

In the case where the correlation term in (2) does not vanish, which it does not in general, we have, assuming the time-average forces per unit mass to be derivable from a time-average potential V,

$$\frac{\partial}{\partial x_k}\int\frac{dp}{r}+\frac{\partial V}{\partial x_k}=\frac{1}{rT}\int_0^T h_k(t)s(t)dt,\ (k=1,2,3). \tag{6}$$

The right-hand side is evidently derivable from a potential

$$R=\int\frac{dp}{r}+V+c \tag{7}$$

where c is an integration constant. Let us call R the *correlation potential.*

For example, for the case of Maxwellian statistics $p=rkT/m$ so that

$$R=\frac{kT}{m}\log r+V+c. \tag{8}$$

If R is, in any case, independent of r then

$$r=r_0\,e^{m(R-V)/kT} \tag{9}$$

and if R vanishes the law becomes the classical one.

In the case of an almost degenerate Fermi gas we have, when the weight factor = 2,

$$p=\frac{8\pi h^2}{15m}\left(\frac{3r}{8\pi m}\right)^{5/3}+\frac{2m\pi}{9h^2}\left(\frac{3r}{8\pi m}\right)^{1/3}(2\pi kT)^2 \tag{10}$$

so that

$$R=\frac{4\pi h^2}{3m}\left(\frac{3}{8\pi m}\right)^{2/3}r^{2/3}-\frac{m\pi}{9h^2}\left(\frac{3}{8\pi m}\right)^{1/3}(2\pi kT)^2\,r^{-2/3}+V+c \tag{11}$$

or solving for r if R is independent of r

$$r=\frac{8\pi m^4}{3h^3}\left[(R-V-c)+\sqrt{(R-V-c)^2+\frac{1}{3}\left(\frac{\pi kT}{2m}\right)^2}\right]^{3/2} \tag{12}$$

For a completely degenerate gas this becomes

$$r=\frac{8\pi m^4}{3h^3}\cdot 2^{3/2}\,(R-V-c)^{3/2}$$

and if R vanishes we get the law used by Thomas and Fermi.

The unmodified form of the distribution law for the case of Maxwellian statistics is used in the well-known Debye-Hückel theory of electrolytic solutions. The theory is also roughly approximate except when applied to extremely dilute solutions. Changes in the results by corrections made in order to take care of the analytical approximations do not lead to com-

pletely satisfactory results. In concentrated solutions of electrolytes, when the ions are crowded together, correlation forces arising from systematic interaction of the ions are to be expected to occur, and then the fundamental equation obtained by eliminating the time-average charge density between a time-average Poisson's equation and the distribution law will be modified by a correlation potential. The no doubt important alterations due to this modification will have to be taken into account in any satisfactory extension of the Debye theory to concentrated solutions. Pauling[3] has shown that by introducing an extra potential in a semi-empirical way it is possible to get results giving the major features of the behavior of electrolytic solutions up to rather high concentrations. The present work indicates the probable physical nature of the effects requiring deviations from the simple Debye treatment and gives a physical interpretation to Pauling's method of correction.

[1] Thomas, *Proc. Camb. Phil. Soc.*, **23**, 542–8 (1926).

[2] Fermi, *Z. Physik*, **48**, 73–9 (1928).

[3] Pauling, paper read at Los Angeles meeting of the American Chemical Society, June, 1925.

THE CRYSTAL STRUCTURE OF POTASSIUM SULPHATE

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Communicated September 5, 1928

In a previous paper[1] the space group of potassium sulphate was determined from data obtained from Laue photographs to be $2Di$-13. While from the point of view of descriptive crystallography this result is of fundamental importance, for crystal structure determinations it is of value only if it can lead to a solution of the complete internal structure of this substance. This paper is a brief account of the way in which the information obtained from the geometrical theory of space groups has resulted in a complete solution not only of the crystal structure of potassium sulphate but also presents for the first time a quantitative three-dimensional structure for the potassium sulphate molecule. Furthermore, the results of x-ray powder photographs of potassium sulphate are presented, and the diffraction effects computed from the structure obtained from the space group are shown to be quantitatively verified in every detail by experiment.

As was previously shown,[1] the elementary lattice of potassium sulphate contains four molecules of K_2SO_4 and has the lattice constants $a_0 = 5.746$ A.U., $b_0 = 10.033$ A.U. and $c_0 = 7.443$ A.U., as determined by Ogg and Hopwood. The author of this paper redetermined the lattice constants

of potassium sulphate by the powder method of analysis and found them to be $a_0 = 5.771$ A.U., $b_0 = 10.064$ A.U., $c_0 = 7.518$ A.U. and has incorporated them in this investigation. Since potassium sulphate is known to be ionized in solution into K^+ positive ions and $SO_4^=$ negative ions and since other inorganic crystals which can be grown from ionic solutions have been shown to preserve their ions in the crystal structure,[2] we can, for a first approximation, consider that the volume included within the elementary rhomb contains eight potassium ions which can be considered as diffracting centers and four SO_4 ions. If these SO_4 ions have a symmetrical structure they, too, can be considered as a first approximation to be diffracting centers.

The simplest structure which has been proposed for the SO_4 group is that suggested by Bradley[3] in which the sulphur is located at the center of a regular tetrahedron whose corners represent the oxygen atoms. This tetrahedral structure has been used by Wasastjerna[4] in his study of the structure of anhydrite and he concludes that in $CaSO_4$ the edge of this tetrahedron is approximately 2.7×10^{-8} cm. Since we have no reason to suppose that one of these SO_4 ions is different from any other one and since the potassium ions are presumably identical chemically it is natural to suppose that they are also geometrically equivalent. These suppositions outlined above simplify the problem into finding the coördinates for two sets of equivalent points falling under space group $2Di$-13. A reference to the analytical expression of the results of the theory of space groups[5] indicates that the potassium ions will have the general positions,

$$x, y, z;\ x + \tfrac{1}{2}, \tfrac{1}{2} - y, \bar{z};\ \tfrac{1}{2} - x, y + \tfrac{1}{2}, \bar{z};\ \bar{x}, \bar{y}, z;$$
$$\tfrac{1}{2} - x, \tfrac{1}{2} - y, z;\ \bar{x}, y, z;\ x, \bar{y}, z;\ x + \tfrac{1}{2}, y + \tfrac{1}{2}, \bar{z}$$

and that the S atoms can have any one of the four following special positions,

TABLE 1

(*c*)	$\frac{1}{4}\ \frac{1}{4}\ 0;$	$\frac{3}{4}\ \frac{1}{4}\ 0;$	$\frac{1}{4}\ \frac{3}{4}\ 0;$	$\frac{3}{4}\ \frac{3}{4}\ 0$
(*d*)	$\frac{1}{4}\ \frac{1}{4}\ \frac{1}{2};$	$\frac{3}{4}\ \frac{1}{4}\ \frac{1}{2};$	$\frac{1}{4}\ \frac{3}{4}\ \frac{1}{2};$	$\frac{3}{4}\ \frac{3}{4}\ 0$
(*e*)	$0\ u\ v;$	$0\ \bar{u}\ v;$	$\frac{1}{2}, \frac{1}{2} - u, \bar{v};$	$\frac{1}{2}, u + \frac{1}{2}, \bar{v}$
(*f*)	$u\ 0\ v;$	$\bar{u}\ 0\ v;$	$\frac{1}{2} - u, \frac{1}{2}, \bar{v};$	$u + \frac{1}{2}, \frac{1}{2}, \bar{v}$

When these various possibilities are checked against the experimental results it is soon observed that the following structure gives the best agreement.

TABLE 2

POTASSIUM NUCLEI

This structure when translated by $\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$ gives the following positions:

$0\ 0\ 0;\ \frac{1}{2}\ 0\ \frac{1}{2};\ 0\ \frac{1}{2}\ \frac{1}{2};\ \frac{1}{2}\ \frac{1}{2}\ 0;$
$0\ 0\ \frac{1}{2};\ \frac{1}{2}\ 0\ 0;\ 0\ \frac{1}{2}\ 0;\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$

SULPHUR NUCLEI

when $u = \frac{1}{4}, 0 = 0, v = \frac{1}{4}$

Substituting these values in (f) changed to

$$u\,0\,v;\ \bar{u}\,0\,\bar{v};\ \tfrac{1}{2} - u, \tfrac{1}{2}, \bar{v};\ u + \tfrac{1}{2}, \tfrac{1}{2}, v$$

and translating as for potassium, results in the positions,

$$0\,\tfrac{1}{4}\,\tfrac{1}{4};\ \tfrac{1}{2}\,\tfrac{1}{4}\,0;\ 0\,\tfrac{3}{4}\,0;\ \tfrac{1}{2}\,\tfrac{3}{4}\,\tfrac{1}{2}$$

The next step is to determine the orientation of the oxygen nuclei with respect to the sulphur and fix their coördinates within the elementary lattice. Since the oxygen atoms are all alike and form the outside shell of the SO_4 group, we should expect the two potassium ions to be symmetrically arranged with respect to the oxygen and sulphur atoms. The simplest arrangement of this kind is shown in figure 1 in which each potassium ion is equidistant from two oxygens and the two potassium ions and the sulphur lie on the same straight line or axis of the molecule. A study of this structure also indicates that the lines joining the oxygen atoms numbered (1), (3) and (2), (4) pass through the molecular axis and are perpendicular to it.

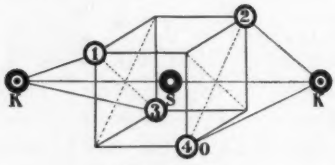

FIGURE 1
The potassium sulphate molecule.

Combining this arrangement with that listed in table 2 suggests the following coördinates for the sixteen oxygen nuclei.

TABLE 3

(0.00, 0.15, 0.30);	(0.25, 0.35, 0.50);	(0.00, 0.15, 0.70);	(0.25, 0.35, 0.00)
(0.50, 0.15, 0.20);	(0.50, 0.15, 0.80);	(0.75, 0.35, 0.00);	(0.75, 0.35, 0.50)
(0.00, 0.65, 0.20);	(0.00, 0.65, 0.80);	(0.50, 0.65, 0.30);	(0.50, 0.65, 0.70)
(0.25, 0.85, 0.00);	(0.25, 0.85, 0.50);	(0.75, 0.85, 0.00);	(0.75, 0.85, 0.50)

The tetrahedral structure as computed from the oxygen positions of the SO_4 ions gives the edges of the tetrahedron as 3.02, 2.89, 2.72, 2.72, 2.72, 2.72 A.U., which is in close agreement with that as computed for $CaSO_4$.[4]

If this structure is correct, then the complete diffraction effects computed by the structure factor for this model must agree with those obtained by experiment. In table 4 these observed and calculated values are listed. The powder photographs were obtained on a General Electric powder diffraction apparatus using a fine slit and exposing for forty hours. Column one gives the estimated intensity; column two, the observed angle; column three, the plane spacing d_{sij} observed; column four, d_{sij} calculated; column five, the indices of the planes. Many of the absent planes which are absent both on the plates and also absent by the diffraction

TABLE 4

THE CALCULATED AND OBSERVED PLANE SPACINGS OF POTASSIUM SULPHATE ORTHORHOMBIC AXES $a_0 = 5.771$ A.U., $b_0 = 10.064$ A.U., $c_0 = 7.518$ A.U. WAVE-LENGTH 0.712 A.U. MOLYBDENUM TARGET

INTENSITY OBSERVED	ANGLE OBSERVED	D × 10^{-8} OBSERVED	D × 10^{-8} CALCULATED	INDICES OF PLANES
None		Absent	Absent	100
None		Absent	Absent	010
None		Absent	Absent	001
None		Absent	Absent	110
None		Absent	Absent	011
None		Absent	Absent	101
30	4° 52′	4.19	4.17	111
25	5° 26′	3.76	3.76	002*
10	6° 03′	2.99	3.01	022β
90	6° 48′	3.01	3.01	022
100	7° 05′	2.89	2.89	200*
5	7° 38′	2.68	2.71	131
30	8° 08′	2.52	2.52	040*
None		Absent	Absent	120
None		Absent	Absent	102
None		Absent	Absent	012
None		Absent	Absent	201
40	8° 26′	2.43	2.50	220
40	9° 12′	2.23	2.29	202
None		Absent	Absent	301
50	9° 50′	2.08	2.09	042
5	10° 07′	2.02	2.08	222
5	10° 30′	1.95	1.90	240
30	11° 01′	1.86	1.88	004
			1.84	151
None		Absent	Absent	232
None		Absent	Absent	314
15	11° 37′	1.77	1.76	024
30	12° 12′	1.68	1.69	242
20	12° 41′	1.62	1.63	331
25	13° 27′	1.57	1.57	204
5	13° 38′	1.51	1.51	044
None		Absent	Absent	521
None		Absent	Absent	093
5	13° 46′	1.49	1.50	224
30	14° 17′	1.44	1.44	400*
5	14° 44′	1.38	1.39	420
20	15° 14′	1.36	1.35	402
10	15° 51′	1.30	1.33	244
5	16° 06′	1.28	1.30	422
None		Absent	Absent	322
15	16° 40′	1.24	1.25	440
5	17° 06′	1.21	1.22	353
10	17° 37′	1.18	1.19	442

TABLE 4 (*Continued*)

INTENSITY OBSERVED	ANGLE OBSERVED	D × 10^{-8} OBSERVED	D × 10^{-8} CALCULATED	INDICES OF PLANES
15	18° 05′	1.15	1.15	264
			1.12	046
			1.11	424
10	19° 00′	1.09	1.09	460
10	19° 47′	1.05	1.05	462
			1.05	246
			1.04	444
10	20° 40′	1.02	1.02	355
10	21° 07′	0.99	1.00	533
			0.99	551
5	21° 35′	0.97	0.97	0, 10, 2
			0.95	266
			0.95	2, 10, 0
			0.95	406
			0.94	464
5	22° 40′	0.92	0.93	426
			0.93	553
			0.92	2, 10, 2
			0.91	515
None		Absent	Absent	285
None		Absent	Absent	372
None		Absent	Absent	152
None		Absent	Absent	235
None		Absent	Absent	493

data are not listed but a sufficient number are given to indicate the type. Those planes marked with an asterisk were used in determining the lattice constant. A consideration of this table shows that *every plane which should give total interference on the model is absent on the photographs and every plane which should be present is present and has the correct spacing.*

The results of this investigation show, for the first time, the complete determination of the crystal structure of potassium sulphate. The elementary lattice of this salt has been clearly determined by the powder method of crystal analysis and found to agree, within less than one per cent, with determinations made by reflection measurements[6] on a rotated crystal. The fact that the SO_4 ion is an entity of the molecule and maintains its tetragonal structure, irrespective of any compound of which it is a constituent, is of striking importance and is further supported by the works of Bradley[3] and Wasastjerna.[4]

In conclusion, the writer takes great pleasure in expressing his thanks to Mr. Jared K. Morse for his interest and helpful suggestions in carrying out this investigation.

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[2] Bragg, W. H., and W. L., *X-Rays and Crystal Structure*, **1924.**

[3] Bradley, A. J., *Phil. Mag.*, **49**, 1225, 1925.

[4] Wasastjerna, J. A., "Structure of Anhydrite. Structure of the Sulphate Group," *Soc. Sci. Fennica Commentationes Phys.-Math.*, **2**, No. 19–30, 1927.

[5] Wyckoff, Ralph W. G., *The Analytical Expression of the Results of the Theory of Space Groups*, **1922.**

[6] Ogg, A., and Hopwood, F. Lloyd, *Phil. Mag.*, **32**, 518, 1916.

FURTHER EXPERIMENTS IN MICROBAROMETRY

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Communicated August 21, 1928

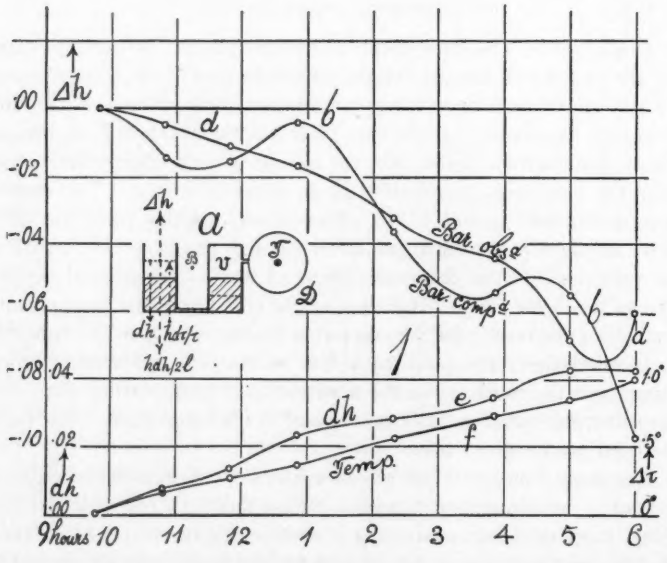
1. *Disc of Air.*—The experiments of my last paper,* in which the expansion of the closed disk-like air volume above one pool of the U-gage is measured while the other is open to the atmosphere, were successively modified to advantage as follows: In the first place a horizontal hole 7 cm. long and 0.6 cm. in diameter was drilled into the iron body of the gage symmetrically between the two pools as indicated at B, figure 1, insert a. This received a thermometer reading to 0.01°C. Thus it was possible to obtain all the terms on the right of the equation $\Delta h = dh + h\,(dh/2l + d\tau/\tau)$ with apparent precision (dh the observed change of level, l the normal depth of the disc of air, h the mean barometer height and τ absolute temperature). Nevertheless, the results for Δh computed in this way were at times too large, at other times too small by a few tenths of a millimeter, showing that there was too much lag in the penetration of temperature, even when the temperature variations did not exceed 0.1°C. per hour. The actual results need not be given here.

2. *Auxiliary Volume.*—The obvious cure for this consists in enlarging the volume v by connecting it with a Dewar flask (D, Fig. 1, insert a) of relatively large capacity, containing a sensitive thermometer at its center T. In this way not only is the τ found for the main body of air, but the importance of the term $hdh/2l$ is virtually eliminated. With a flask of 450 cm.[3] capacity, if this volume is reduced to a cylinder of the diameter 9.4 cm. of the gage, the disc volume of the gage and the reduced volume of connections added, the term becomes $hdh/16$ instead of $hdh/3$. For so thin a medium as air and slow procedure, the Dewar flask is of little advantage, and any glass vessel will do equally well. Thus, on comparing the temperature change $\Delta\tau$ of thermometer on the barometer with that in the Dewar flask, the relations in successive runs on different days were

	JULY 12	JULY 13	JULY 14	JULY 19
Time	9 hours	7 hours	7 hours	8 hours
Barometer	$\Delta\tau = 0.8$	0.5	0.8	0.5°C.
Dewar	$\Delta\tau = 1.0$	0.2	0.7	0.8°C.

Values of $\Delta\tau$ should never exceed this, implying a room of fairly constant temperature.

Data. —As the Dewar flask is here joined on the right (Fig. 1, *a*, *D*), to the closed volume v, and as the micrometer reading increases when this surface of the gauge is depressed, furthermore, as $d\tau/\tau$ is always positive, dh, $hdh/2l$, $hd\tau/\tau$ are additive, while Δh is positive if dh is negative. Again, since dh is positive when Δh is negative, dh and $hdh/2l$ will have opposite signs to $hd\tau/\tau$ and the difference is to be taken. Δh of course indicates the barometric change on the left or open side of the gauge. These relations are suggested in figure 1, *a*.



In the graphs, figure 1, the abcissas give the hours at which observations were made. Curve *d* summarizes the observed (to 0.01 cm.) barometer height reduced to 20°C. Curve *b* is the change of barometer, Δh, computed from the interferometer observations. For this purpose curve *e* gives the values of $dh = 0.71\, dr_0$ (r_0 read off to 0.0001 cm. at the micrometer) and curve *f* the changes of temperature (read to 0.01°C.) in the Dewar flask.

Figure 1 is a good example of the more complete series, made between 9 A.M. and 6 P.M. The total change of temperature ($d\tau$) of the Dewar flask is here fully 1°C. (curve *f*). The micrometer displacement dh has increased over 0.04 cm. But the curves *b* and *d* are an attempt at coincidence, remembering that the data *d* (reduced to 20°C.) can be read but to 0.01 cm. This curve is really a ribbon of a breadth of about 0.0025 either

side of the middle and the curve b is liable to be a trustworthy result within a few 0.001 cm.

These experiments were carefully made after a variety of other similar preliminary work. They did not come out as well as was expected, but they are a great improvement on the preceding set without flask. Obviously a thermocouple will have to be used for temperature measurement. If the trustworthiness of such a curve as figure 1b can be slightly increased, the vessel should make an available laboratory for treating small pressure increments, Δh in chemical reactions, for instance. In fact, if both shanks of the U-gauge are closed and provided with identical auxiliary flasks, the equation becomes $\Delta h = dh + h(dh/l + (d\tau' - d\tau)/\tau)$, in which temperature changes are active differentially.

* These PROCEEDINGS, **14**, 1928, pp. 641–45.

REFLECTION OF SOFT X-RAYS

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Communicated September 8, 1928

A. H. Compton[1] has called attention to the fact that since the index of refraction in the hard x-ray region is less than one, total reflection should occur. This prediction has been verified by him and others, and good agreement found with the Drude-Lorentz theory by which

$$\mu = 1 - \frac{e^2 n}{2\pi m} \sum \frac{n_c}{\nu^2 - \nu_c^2}$$

where n is the total number of atoms per cc., n_c the number of electrons per atom having the critical frequency ν_c, and the other symbols have their usual significance. It was the purpose of the experiments described here to investigate reflection in the region of long wave-length x-radiation. The problem is complicated experimentally and theoretically by the high absorption, the non-monochromatic nature of the ordinary source of radiation, and the lack of exact information concerning the critical frequencies in the region. Holweck[2] found a small amount of reflection from a bronze mirror at angles 11° and 16°. One[3] of us showed by a photographic method that this type of radiation is specularly reflected from glass, copper and nickel over quite a range of angles, but this method did not lend itself to a quantitative measure of intensities.

The apparatus consisted of an x-ray tube with nickel target connected

by a slit system to a chamber which contained the mirror. The radiation passing through the slits fell on the mirror and was reflected to a receiving plate. The photoelectric emission from this plate served as a measure of the amount of radiation reflected. The mirror was capable of rotation about an axis perpendicular to the beam. The angular position of the mirror could be read to 6′. The angular width of the beam was approximately 25′. No wax joints nor stopcocks were on the apparatus side of the diffusion pump. Tests showed that the slits prevented corpuscular radiation from reaching the measuring system. The photoelectric current was measured by the rate of deflection of a Swann electrometer used at a

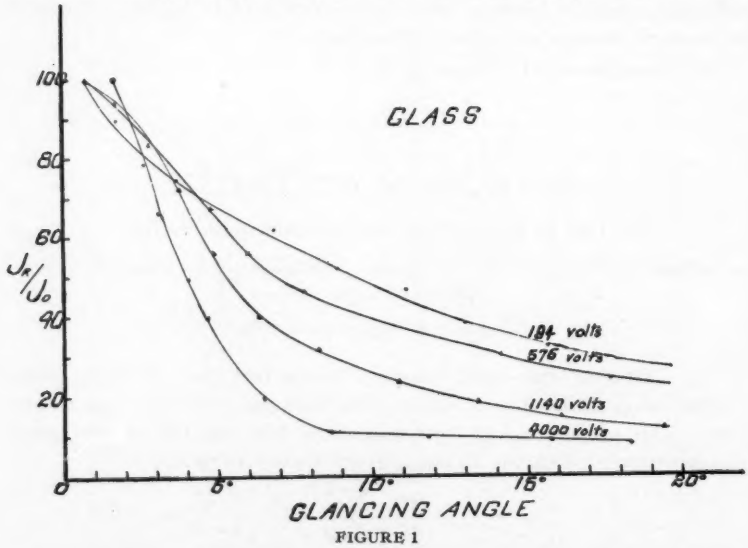

FIGURE 1

sensitivity of about 2500 mm./volt. Two mirrors were used, one of highly polished iron and the other of optically flat glass. While the apparatus was being baked at 500°C. with the iron in place a slight leak developed, hence the surface may have been iron oxide. A more complete description of the apparatus, experimental method and results will be published later.

The results for the reflecting power of glass are shown in figure 1 and for iron in figure 2. The coördinates are per cent reflection J_r/J_o and glancing angle. At position 0° the whole beam of radiation fell directly on the receiving plate; at 2° for iron, and at a little smaller angle for glass, the beam fell completely on the mirror. It is evident that there is no total reflection, sharply defined, such as occurs in the hard x-ray region with the possible exception of the 4000 volt radiation reflected from glass. The

Drude-Lorentz formula predicts a critical angle of a little less than 1° for this. For the other voltages the critical angle would be greater. In fact the longer the wave-length of the radiation, the less is reflected by the glass at small angles. The high voltage curve crosses through the curves for lower voltages until at large angles they are in reverse order.

An outstanding property of soft x-rays is their extremely high absorbability. Prins[4] has recently called attention to the effect of absorption on the reflecting power near an absorption edge in the hard x-ray region. It will be seen that the explanation of our results with glass is found in tak-

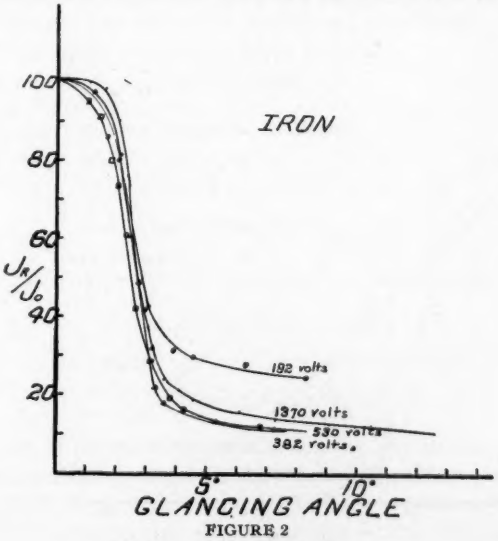

FIGURE 2

ing into account the absorption. The Fresnel formula for reflecting power, where the complex index of refraction

$$n = 1 - \delta - i\,k$$

is inserted, was used to compute the points of figure 3. In this $1 - \delta$ is the usual index of refraction, and k is connected with the usual absorption coefficient (μ) by $k = \mu\lambda/4\pi$. A value for k for radiation produced by a potential difference in the neighborhood of 576 volts was computed from an absorption coefficient obtained by one[5] of us earlier at 500 volts, as 0.0006; and in the neighborhood of 200 volts as 0.011. At 4000 volts the value 7×10^{-6} was taken as probable by comparison with values for aluminum and oxygen. In extrapolating the absorption was assumed to vary as $\lambda^3 Z^4$. As the radiation was the general radiation for the voltage

used, the value of λ to be assumed is uncertain. δ was computed from the Drude-Lorentz formula at 34 Å as 0.004 neglecting critical frequencies, and as 0.0034 using available information concerning them. 0.004 was used with the value of k in the neighborhood of 576 volts in obtaining curve B. At 90 Å similarly the values 0.028 and 0.0163 were found for δ and were used with the value of k in the neighborhood of 200 volts to obtain curves C and D. Curve D fits the experimental facts for 192 volts better.

A, figure 3, is a theoretical curve for $\delta = 0.004$ and absorption negligible, ($k = 0$). This curve exhibits the total reflection observed in the hard

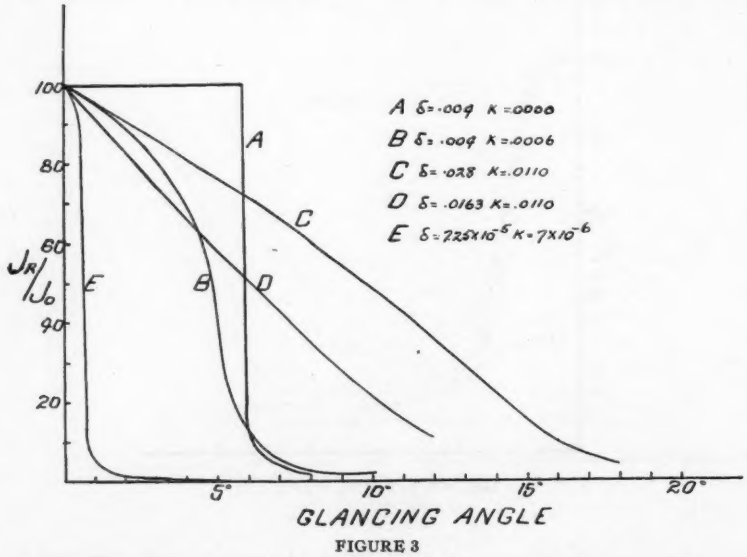

FIGURE 3

x-ray region where absorption is negligible. Curve B for the same δ but the estimated value of k shows the marked effect of the absorption term. The effect is to cause an immediate falling off in reflecting power with increasing glancing angle such as was observed experimentally. All the curves are of the same general type as the corresponding experimental ones, and the values of the reflecting power are of the right order of magnitude. The experimentally observed crossing of the curves is also exhibited by the theoretical curves. The major differences between the theoretical and experimental curves occur at large angles where the experimental curves all lie above the theoretical. We have neglected in calculation the fluorescent and scattered radiation from the mirror itself which would be measured as well as the reflected radiation. Also the beam is not mono-

chromatic but contains considerable radiation of longer wave-length than that assumed in computation. These factors would all tend to keep the experimental curves above the theoretical curves at large angles.

In the case of iron δ would be expected to be larger than for glass. In practice the reflecting power falls off more rapidly than for glass. No value of k was found which would explain this. If the surface is assumed to be iron oxide, δ would be about the same as for glass, and k much larger. This would fit the results better. Because of some uncertainty about the surface extensive computations have not been made on iron. It is our intention to repeat the experiment using a metallic mirror deposited upon an optical flat surface in order to determine whether these curves are characteristic of the metal or due to surface conditions.

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[5] Laird, *Ann. d. Phys.*, **46**, 605 (1915).

FLUORESCENCE AND SOLID SOLUTION[1]

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Communicated August 18, 1928

Fluorescence in an inorganic solid is usually ascribed to the presence of a trace of activating metal in solid solution. There is however at least one class of pure chemical compounds, namely, the uranyl salts, which form an exception to this rule. Here it is the radical UO_2, a definite part of the compound, which is responsible for the fluorescence. At ordinary temperatures the emission spectra of such compounds under ultra-violet excitation consists of about seven equally spaced broad bands extending throughout the whole visible range.

But uranium may also serve in the rôle of activating metal: so that when uranium is known to be the cause of fluorescence there are two possibilities. A uranyl compound may be present, in which case we would expect the characteristic many-banded spectrum, or it may be that the uranium is in small amounts as an activator, in which case the spectrum might have any other form.

In a recent study[2] it has been shown that several substances can be activated by traces of uranium. Many of these preparations have a continuous spectrum, or one composed of two or three very broad overlapping bands which are unresolved at the temperature of liquid air.

Solutions in the alkali fluorides form marked exceptions, however, both in the brightness of their luminescence and the resolved character of their spectra.

Sodium fluoride with small amounts of uranium gives a vivid yellow fluorescence. With lithium fluoride the color is a bright blue-green. Potassium fluoride brings out the orange, but this salt deteriorates rapidly, due to its hygroscopic nature.

In contrast with most fluorescent preparations the lithium fluoride and sodium fluoride fluorophors are very simply made and in addition are exceptionally stable. To prepare a small amount of sodium fluoride, for instance, a loop of platinum wire is used on which to form a molten bead in the gas flame. A very small speck of uranium in any form is touched to the bead and the whole returned to the flame and held in the molten condition until the uranium has dissolved. On cooling the bead to room temperature and exciting it by ultra-violet light the bright yellow fluorescence appears, unlike the green characteristic of the uranyl salts and much brighter than even the brightest of them. The condition of the

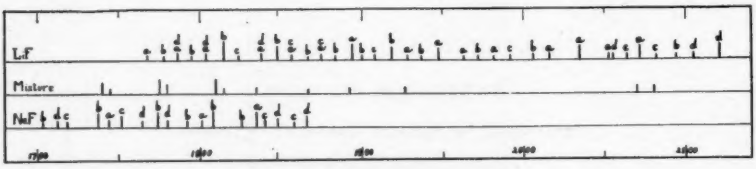

FIGURE 1

flame, whether oxidizing or reducing, the length of time of heating after solution is complete and the rate of cooling are without noticeable influence on the resulting fluorescence. The only requisite is that the sodium fluoride be molten a sufficient length of time to dissolve the uranium.

Excitation at the temperature of liquid air gives a spectrum resolved into many fine line-like bands whose locations are independent of the amount of activator present. So sensitive is the sodium fluoride to the presence of uranium, that one part in ten million gives an easily measurable fluorescence. In fact, a method of spectroscopic detection of uranium[3] has been based on the formation of this fluorescent material, the activating action being apparently unaffected by the presence of other materials.

Figure 1 shows the positions and relative intensities of the lines emitted at the temperature of liquid air. Their exact location as determined from an average of several measurements, both photographic and visual, will be given in a paper, now in preparation, on uranium as an activator. Astronomical green-sensitive plates, obtained from the Eastman Kodak Co., were used in making the photographs.

These lines can be arranged in four sets of constant frequency separation with a slightly different interval for each set. The members are labeled in the figure. Sets *A*, *B*, *C* and *D* have the frequency intervals 17.9, 17.6, 17.2 and 16.7 units, respectively.

Figure 1 shows also the location of the lines in lithium fluoride obtained with the specimen at liquid air temperature. These can be arranged in four sets of the same separation as those for sodium fluoride. Three of the sets are slightly displaced from the sodium fluoride positions, but Set C with the 17.2 interval is identical with that of sodium fluoride. There is, in fact, one coincident line. The average of these frequency intervals is 17.6, the Tanaka[4] interval for uranium. All of these intervals are expressed in units of ten times the reciprocal centimeter.

The meaning of constant frequency emission for a solid is rather obscure. For gaseous molecules both rotation and rotation-vibration spectra have a constant frequency system, the size of the interval dependent upon the moment of inertia. The four different intervals here are probably also dependent upon vibrating systems of slightly different moments of inertia, though the cause of these differences is as yet uncertain.

For both lithium fluoride and sodium fluoride we have the uranium presumably in solid solution in a single crystalline compound. It is conceivable that the introduction of the uranium might produce a measurable change in the crystal structure of the solid solvent which surrounds it. To test this, samples were made containing the maximum amount of uranium for good fluorescence: about one part in two hundred. X-ray diffraction photographs were then taken using the powder method. Side by side on a single photograph the patterns due to the solid solvent containing the uranium and the pure, non-fluorescent sample could be seen. For neither fluoride did the diffraction lines show any difference produced by the addition of uranium. By direct visual observation the lines had the same intensity, width and position. And, moreover, there were no additional lines to indicate the presence of a new crystalline compound, nor was there an increase in the general blackening. This result is in contradiction of the view put forth by J. Ewles,[5] who predicted that the addition of an activating metal causing fluorescence would cause a change in the crystal lattice of the solvent.

One possible physical picture of the way in which the uranium is taken into solid solution might in some part explain the lack of change, and reconcile the prediction of Ewles with the results found here. The most obvious way in which the uranium might go into uniform solid solution is for it to replace a lithium atom here and there in the lattice. At first hand it would seem that the much heavier uranium atom would also be a much larger one, and by replacing lithium or sodium would necessarily produce a deformation in the lattice. However, on consulting the graph of atomic

volumes in Sommerfield's "Atomic Structure and Spectral Lines," it is seen that uranium, although over thirty times heavier than lithium, has an atomic volume slightly smaller. It is, in fact, only half as large as sodium. It could scarcely be expected then to produce a noticeable deformation, especially when it is present as such a small percentage of the whole.

It has repeatedly been put forward that a resolved fluorescence spectrum is possible only when the fluorescing material is in the crystalline state. If this is true, we would expect that any change in the crystalline state would bring about a change in the spectrum. In the fluoride fluorophosphors we have a single solvent with a perfectly definite and measurable crystal structure and an equally definite measurable fluorescence spectrum. They might well be used for testing the above supposition.

One way of changing the lattice constant of a medium is by the addition of a substance with which it is isomorphous. Both lithium fluoride and sodium fluoride are cubic, lithium fluoride with an edge[6] of 2.007 ± 0.004 Å and sodium fluoride with a cube edge of 2.310 ± 0.004 Å. Mixing the two salts and cooling the melt might yield a mixture with a grating constant intermediate between the two. The work of Travniček[7] with the calcium strontium sulphide samarium mixed phosphors, in which he showed the relation between the grating constant and the position of the band of maximum phosphorescence for phosphors of varying composition, suggests that the attempt is not entirely hopeless.

Accordingly, samples were weighed out containing one-tenth, two-tenths, five-tenths, and one gram of lithium fluoride to one gram of sodium fluoride. All of the mixtures contained the same proportion by weight of uranium, approximately one to two thousand, the amount required for maximum fluorescence in sodium fluoride. Beads were made on platinum wire and for each composition a large number of them were put together on a black background for excitation and viewing in the spectroscope.

To the eye the fluorescence of the mixture is seen to be slightly changed. The brightness is about the same, but the color is more greenish, increasing, as would be expected, as the amount of lithium fluoride in composition is increased. The spectrum extends from the orange through the blue-green, including the range of both components. At the temperature of liquid air the yellow end has a continuous background on which are superimposed some poorly resolved lines corresponding to the strongest ones of sodium fluoride. Photographs, measured both with a recording densimeter and a visual micrometer show that they are shifted in position, the amounts varying for different lines. The lithium fluoride lines, best seen in the one-to-one sample, are found to be very slightly shifted in position and are better resolved than those due to the sodium fluoride. The surprising thing is that the positions of the bands are the same for the mixtures of all different proportions. The only thing that varies as we go from the

one-tenth lithium fluoride to equal parts of lithium fluoride and sodium fluoride is the increase in the intensity of the lithium fluoride lines.

The fluorescence of the mixture has been represented by the center group of lines in figure 1. Some of the sodium fluoride lines are apparently unshifted. The brightest ones show a change of about 3 Å toward shorter wave-lengths. Those due to the lithium fluoride show a much slighter shift in the opposite direction.

After the spectroscopic examination a small amount of each composition was removed for crystal study. X-ray diffraction photographs were made, comparing on each film the fluorescent sodium fluoride with the fluorescent mixture of a certain composition. From these photographs it could easily be seen that the diffraction lines due to sodium fluoride have been shifted by the addition of lithium fluoride, in such a direction as to indicate a decrease in the length of the cube edge. Again, as in the fluorescence, the amount of the shift was the same for all compositions. Apparently, in each case, instead of crystallizing together in all proportions, as the strontium calcium sulphide of Travniček, a small amount of lithium fluoride had entered into the sodium fluoride structure, and the rest had crystallized by itself. Repeated measurements with great precision showed the change to be from 2.310 Å to 2.301 Å, a shrinkage of approximately 0.01 Å unit. Although this seems to be a small amount it is easily detected on the diffraction photographs. At first it appeared that the sodium fluoride had not produced a corresponding change in the lithium fluoride but an exposure of a sample of one-tenth gram of sodium fluoride and one gram of lithium fluoride, on the same film with pure lithium fluoride, and five times the usual number of hours, showed that the lithium fluoride has been stretched slightly by the sodium fluoride, about 0.005 Å. The shifted sodium fluoride lines were also present, indicating that there was an excess of sodium fluoride, and that 0.005 Å was the maximum stretch possible under these conditions. The change in the lithium fluoride was only half that of the change in the sodium fluoride, both in regard to the position of the emission bands and the length of the cube edge.

There is, then, a very simple relation indicated. An increase in crystal dimensions causes an increase in the wave-length of the fluorescence emission. This is an agreement with the colors observed in the fluorescence of the simple fluorides. In order of size of lattice we have lithium fluoride, 2.007 Å, sodium fluoride, 2.310 Å and KF a 0.664 Å. Their fluorescence colors are respectively green, yellow and orange.

Although these results with uranium as the activator are perfectly definite and consistent among themselves, they are in direct contradiction to the results found by Travniček with samarium. As the lattice of the calcium strontium sulphide mixture increased from 2.834 Å to 2.997 Å, the brightest band was shifted from 6059 toward the blue to 6036. Thus,

an increase in crystal dimensions causes a decrease in wave-length of the phosphorescence.

The key to the solution of this discrepancy lies no doubt in the different electron configurations of the activators themselves. The rare earth group, of which samarium is a member, is generally considered to have its valence electrons on an inside shell, and not on the outside, as is the case with the other elements. The approach of neighboring atoms would naturally be expected to produce a different, perhaps even opposite, effect on these sheltered electrons, than when the electrons responsible for the emission are on the outside and more directly approached. Further experiments with different activators might show whether or not all of the rare earths behave in a like manner in this regard.

[1] This investigation was made under a grant from the Hecksher Fund of Cornell University. It was inspired by previous work with Professor E. L. Nichols on uranium as an activator. The author wishes to acknowledge his continued interest and helpful suggestions during the course of the present work.

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NOTE ON THE LYMAN BANDS OF HYDROGEN

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Communicated September 13, 1928

In a very admirable paper, Hori[1] has carried through a complete and thorough analysis of the rotational terms for the Werner and Lyman bands of hydrogen, using his own new data for the former and the data of Witmer[2] for the latter. Starting out from an analysis of the vibrational levels given by Dieke and Hopfield,[3] he obtains a complete assignment of rotational quantum numbers to all the observed lines of the thirty-two bands and also derives values for the constants in the formulas for the band frequencies. His value of the moment of inertia of the normal hydrogen molecule has received striking confirmation through Dennison's[4] solution of the problem of the specific heat of hydrogen at low temperatures. There remains however some uncertainty regarding the structure of the Lyman bands $(B_3\text{-}A_n)$[5] inasmuch as the identity of the two branches actually observed is not definitely fixed. Without being categorical, Hori favors the interpretation that these bands consist of P, Q and R branches, like

the Werner bands but with the corresponding lines of the P and Q branches happening to lie so close together as to form unresolved doublets throughout the entire system, and has shown that theoretical formulas for the frequencies based on this hypothesis are indeed capable of describing the bands within the limits of experimental error.

If the bands are to be interpreted in this way it is necessary, however, to assume a quite unheard of value for the constant δ which fixes the magnitude of the "sigma-type" doubling. This constant displaces each Q line relative to the corresponding P line so that it lies practically on top of the other instead of in its normal position approximately midway between corresponding P and R lines. To the improbability of such a large doubling constant is added the improbability that even with a large δ the Q and P lines would lie so close together throughout the system of bands as to have completely escaped resolution. The doubt thus cast on Hori's interpretation of the bands is increased by a theoretical analysis of the possible types of molecular states belonging to the B-A system of which the Lyman bands form one progression. In order that the B-A system should contain a Q branch it would be necessary that the upper (B) level be of the "P" type with a unit of orbital electronic angular momentum along the nuclear axis. This follows from the fact that the normal state is an S state while $S \longrightarrow S$ transitions yield only P and R branches. The possibility that the B state is of the P type may, however, be practically ruled out on theoretical grounds. The argument runs briefly as follows: Dieke and Hopfield have extrapolated the vibrational levels of the B series and the C series (upper state for Werner bands) to an approximately common convergence point which may be identified with the energy of a pair of separated H atoms, one of which is in the normal state while the other is in a 2 quantum state. This constitutes strong evidence that both of these molecular electronic levels dissociate adiabatically into such a pair of atoms. Now there are just sixteen possible molecular states which can dissociate in this manner. Eight of these levels, consisting of four approximately degenerate pairs, have a unit of electronic angular momentum along the inter-nuclear axis and are classed as P states. Two of these pairs of states are triplet states and should not combine freely with the normal singlet state. Of the other two, one is "symmetric in the nuclei" in the sense that the electronic wave function for fixed nuclei is symmetric with respect to a reflection in the plane which forms the perpendicular bisector of the internuclear axis. The other is antisymmetric with respect to the nuclei and should not combine with the normal state.[6] Thus, there is only one degenerate pair of states combining freely with the normal state which should yield P, Q and R branches. The Werner bands are undoubtedly produced by such a pair of states. Therefore, to account for three branches in the B-A bands, it would

be necessary to give up the hypothesis that the B and C states are both "two-quantum" states, or to assume that either the Werner system or the B-A system is a singlet-triplet combination not to be expected for such a light molecule.

We have therefore reëxamined the B-A bands to see whether a reinterpretation based on the two branch hypothesis might not be feasible. The analysis is not yet as complete as that of Hori but clearly demonstrates that this alternative interpretation is in satisfactory accord with the data.

When plotted on a ν-j graph, Witmer's data for the twelve bands in the Lyman progressions (B_3-A_0 to B_3-A_{11}) gives smooth parabolas, provided the proper assignments of j-values are found. The assignment of j-values to the lines cannot always be made uniquely for any one band alone, but the plotting of the whole set of curves, taking account of systematic variation of slope, curvature, and position of apex, does afford unique assignments. These are in complete accord with the assignments made by Hori,[7] except that the double interpretation of the P-lines is given up.

Since there is no "sigma-type" doubling for S states, the δ-term of Hori[8] may be dropped. Assuming the expressions:

$$E' = A'h + B'hj'^2 + \beta' hj'^4;\ E'' = A''h + B''hj''^2 + \beta'' hj''^4$$

for the energy of the upper and lower states, respectively, the frequency is:

$$\nu = \frac{E'-E''}{h} = A'-A'' + B' + \beta' + (\pm 2B' \pm 4\beta')j'' + (B'-B'' + 6\beta')j''^2 \pm 4\beta'j''^3 + (\beta' - \beta'')\, j''^4 \qquad (1)$$

the upper sign referring to the R and the lower to the P branch.

The usual methods were employed to obtain values of the constants for the progressions B_0-A_n to B_3-A_n, using Witmer's data for the last and the data of Dieke and Hopfield[9] for the first three. The constants for the lower (A) states are in close agreement with those given by Hori, but the values for the upper states diverge conspicuously, the differences being chiefly due to the fact that the present analysis does not admit of a δ-term in the energy expression, a term for which, as stated above, Hori gets an unusually large value. The experimental values of the constant B', for example, deduced from the present analysis, are 18.4, 18.1, 17.4, and 16.8, for the progressions B_0-A_n to B_3-A_n, respectively, while Hori's value for B'_3 is 12.103. From the latter, Birge[10] has extrapolated the value 13.94 for B_0', using the expression $B_n = B_0 - \alpha n$. The corresponding value for the moment of inertia of H_2 in the B_0-state is 1.99×10^{-40} gm. cm.^{2}, while the present analysis[11] gives 1.51×10^{-40}.

In table 1 are given the wave numbers for the lines of two strong bands observed by Witmer, together with the values calculated from (1) and those calculated by Hori for the R and P branches. (The positive j values

refer to the R branch, the negative to the P branch.) The values used for the constants in (1) are:

	$A'-A''$	B'	B''	β'	β''
B_3-A_4	78805	16.8	47.5	0.05	0.007
B_3-A^7	69764	16.8	38.5	0.05	0.002

Table 2 gives the calculated relative intensities of the lines in the B_3-A_n bands[12] taking into account the 3:1 alternation factor which is one for the first R line and 3 for the first P line. The calculated intensities are based on the approximate formula for rotational thermal equilibrium:

$$I = g\,(\bar{j} + 1/2)\,e^{-E'/kT} \begin{cases} g = 1, 3 \\ \bar{j} = \dfrac{j' + j''}{2} = 1/2, 3/2, \ldots \end{cases} \qquad (2)$$

The assumed temperature of 400° abs. is probably lower than the actual temperature of the discharge. The observed intensities[13] given for comparison are the mean of microphotometer measurements made on new oil-sensitized plates which Professor Lyman has kindly made for us. These measurements are not corrected for the properties of the plates to give accurate intensity ratios, but they do define an ordinal arrangement of

TABLE 1

OBSERVED AND CALCULATED FREQUENCIES

	B_3-A_4			B_3-A_7		
j''	OBS.	CALC.	HORI	OBS.	CALC.	HORI
1/2	78832	78832	78833	69792	69794	69793
3/2	808	806	807	792	785	786
5/2	...	...	...	730	736	733
7/2	...	...	...	633	634	642
− 3/2	703	703	703	683	682	681
− 5/2	545	548	549	562	563	563
− 7/2	330	332	335	397	400	404
− 9/2	056	058	057	196	197	195
−11/2	77731	77730	77721	68955	68959	68950

TABLE 2

INTENSITIES OF EMISSION LINES

	j'	1/2	3/2	5/2	7/2	9/2	11/2	13/2
Calc.	R	..	1.74	8.17	2.84	6.98	1.58	2.74
	P	5.90	3.48	12.28	3.75	8.73	1.90	..
Obs.	R	..	7.3	7.4	1.8	0	0	..
	P	8.5	10.0	6.8	3.4	1.7	0.4	..

the lines as regards intensity which should be very nearly right. The table shows clearly (*a*) that the normal alternating intensity of the H_2 band spectrum is practically absent in the case of these bands; (*b*) that the distribution of the molecules among the different rotational states, quite apart from the alternating effect, is one corresponding to a lower temperature than that which actually exists; (*c*) that there is an intensity

dissymmetry favoring the P branch which has nothing to do with the distribution of population among the different rotational levels. The dissymmetry mentioned under (c) is indicated by comparing the intensities of P and R lines having the same initial state. The disagreement between the theoretical and observed relative intensities of the pair of lines R (5/2), P (9/2) with the common upper level $j' = 7/2$ and the complete absence of higher R lines indicates that the approximate formula (2) is in need of correction. This is not surprising as (2) is known to fail for the infra-red vibration-rotation bands and suitable corrections for the fundamental bands have already been worked out by Kemble[14] and Oppenheimer.[15]

The non-appearance of alternation (a) and the small number of observed lines (b) may both be due to the peculiar method of excitation by which the B_3-A_x bands are produced. As is well known, they are obtained by passing a discharge through a mixture of argon and hydrogen. The fact that under proper conditions, only the B_3-level is excited shows that the excitation process is highly selective, and it has therefore been described as consisting of collisions between excited A atoms and H_2 molecules. It is indeed possible that this process is so sharply selective as to favor not only a single vibrational level but a single one, or at most a very few, of the rotational levels as well. At sufficiently low gas pressures, the trend of the H_2 molecules toward thermal equilibrium while in the excited state could not proceed very far, and this would account for the small number of emission lines. Furthermore, if the most favored rotational level happened to be a "weak" level, i.e., one for which the alternation factor has the smaller value, the population of the weak levels in the excited state relative to the strong levels would be abnormally large and the alternation in intensity would be reduced or even reversed.

A certain amount of support for this hypothesis may be deduced from a detailed consideration of the location of the argon energy levels responsible for the excitation.[3] The excitation energies of these levels in frequency units are 93, 138; 93, 745; 94, 548; 95, 394. The first and third of these are metastable and hence are presumably responsible for the excitation. To determine the exact nature of the excitation one must compare the above energies with the energies required to produce all the various possible transitions between the A_0 and B_3 states disregarding the selection principle for j but counting only "weak to weak" and "strong to strong" transitions. On calculating the various molecular term differences, it is found that the transition whose energy is closest to the 93138 argon level is the one from $j'' = 9/2$ to $j' = 7/2$ with the energy 93086, while the one closest to the 94548 level is $j'' = {}^1/_2$ to $j' = 11/2$ with the energy 94545, both of these transitions being in the "weak" system. The next closest transitions lie about a hundred units away in both cases. However, we must note

that the first transition has an initial state which, due to its high j-value, is not abundantly populated in the gas, while the second involves a large jump in j. Therefore, these transitions will actually be the favored ones only if the excitation function dies off rapidly as the molecular term difference diverges from the exciting term difference. Evidently the situation is quite complicated so that the fact that alternation of intensities is not actually observed does not disprove its existence under normal excitation.

If the bands are produced by the primary excitation of a small number of rotational levels with a subsequent spreading out to other levels by collisions while in the excited state, it is evident that the gas pressure should have a marked effect on the intensities. Experiments to determine this effect are now in preparation.

In the absorption spectrum and in the emission spectrum in pure hydrogen the above complications are not present, and the observed intensities should agree closely with those calculated on the assumption of thermal equilibrium among the initial rotational levels. Unfortunately, the only available observations are visual estimates of Dieke and Hopfield.[16] Due to the large number of overlapping bands in the emission spectrum it is difficult to get good estimates of intensities, while in the absorption spectrum many of the crucial lines are not well resolved. There are however certain lines uniformly strong or uniformly weak throughout all the bands which are in agreement with the assumption of alternating intensities.

The authors are greatly indebted to Professor Lyman and his assistant Mr. Leighton for their help in securing new plates and to the Harvard Observatory which has kindly placed its microphotometer at our disposal.

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[1] Hori, *Zeit. Phys.*, **44**, 834 (1927).

[2] Witmer, *Phys. Rev.*, **28**, 1223 (1926).

[3] Dieke and Hopfield, *Phys. Rev.*, **30**, 400 (1927).

[4] Dennison, *Proc. Roy. Soc.*, **A115**, 483 (1927).

[5] For the nomenclature see Dieke and Hopfield, loc. cit.

[6] A more detailed discussion of the wave mechanics of the excited states of the H_2 molecule will be published shortly by E. C. Kemble and C. Zener.

[7] Hori, loc. cit., p. 842.

[8] *Ibid.*, p. 845.

[9] Dieke and Hopfield, loc. cit., pp. 403 and 407.

[10] Birge, *Proc. Nat. Acad. Sci.*, **14**, 12 (1928).

[11] If we substitute 1.51 for 1.99 in Birge's table 1 (loc. cit., p. 13) we get $I_{0\omega^0} = 2000$ instead of 2640, in much closer agreement with the value 2050 for the A-state.

[12] The calculations were made with the new value of B'. The smaller value of Hori would of course give an even slower decrease of intensity for the outer lines.

[13] The first two R-lines are not resolved in most of the bands.

[14] E. C. Kemble, *Phys. Rev.*, **25**, 1 (1925).

[15] J. R. Oppenheimer, *Proc. Camb. Phil. Soc.*, **23**, 327 (1926).

[16] Dieke and Hopfield, loc. cit., Tables 1 and 3.

SYSTEMATIC VARIATIONS OF THE CONSTANT A IN THERMIONIC EMISSION

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Communicated August 27, 1928

Recent measurements[1] on the thermionic emission from a platinum surface during outgassing have brought to the attention of the writer an empirical relation between the thermionic constants for a metallic surface which was discovered by Richardson[2] for tungsten and platinum in 1915, but which has apparently been completely neglected in formulating the various theories of the emission process. This relation may be stated as follows: In the Richardson-Dushman equation,

$$I = A\,T^2\,e^{-b/T} \qquad (1)$$

whenever the work function, b, of a given surface is changed by any method (such as heating, outgassing, coating, etc.) the constant A also changes in such a way that *log A is a linear function of b.*

As is well known, according to Dushman's theory,[3] A should be a universal constant having a numerical value of approximately 60 amp./cm.^{2} deg.^{2} This conclusion has been confirmed experimentally by Dushman and his co-workers[4] and by Zwikker[5] and Goetz[6] through accurate measurements on a number of clean metals, and has recently received further theoretical justification at the hands of Fowler[7] and Nordheim[8] on the basis of the Sommerfeld electron theory and the wave mechanics. While a number of observers have obtained, under various conditions, values of A differing considerably from the theoretical it has usually been possible to attribute these to the disturbing effects of surface contamination. However, the writer's recent results[1] for platinum (including some still more precise ones as yet unpublished) have shown definitely that it is possible to have a thoroughly cleaned metallic surface exhibiting a value of A 200 times or more greater than 60. Dr. A. Goetz has informed the writer that he has obtained similar results for nickel. The question is therefore raised as to whether some of the observed variations of this "constant" are not of more fundamental nature than had been supposed.

The problem of explaining such variations theoretically has been taken up by a number of writers. Richardson[9] and Wilson[10] were able to explain many results for gas-filled surfaces by assuming the presence of an electric double layer. Bridgman[11] and Langmuir and Tonks[12] related the variations in A to the presence of a surface heat of charging term. However, Davisson and Germer[13] pointed out that such a term should not affect results obtained at constant surface charge and Bridgman[14] later con

cluded that this term in his theory should in fact be zero for all metals. Raschevsky's[15] detailed thermodynamic treatment yields an emission equation which allows for variations in A. Finally, Bridgman,[16] in a very recent paper to be discussed later, shows that all such variations may be simply explained as due to slight variations of b with temperature. None of these theories leads directly to the linear relation between log A and b stated in the first paragraph, which is perhaps not surprising, since this relation, while simple in itself, is the result of very complicated surface phenomena. However, since considerable experimental evidence confirming this relation for many types of surfaces has accumulated in the past

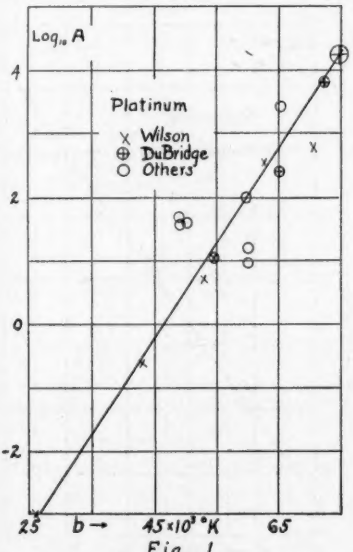

Fig. 1

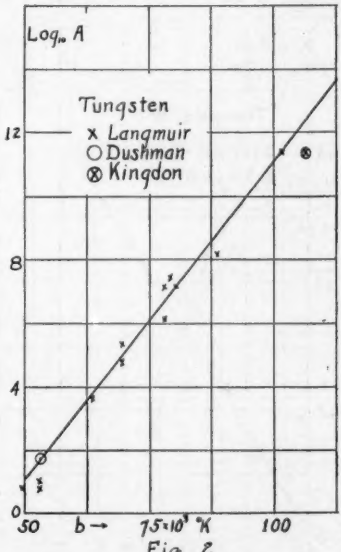

Fig. 2

few years, it seemed worthwhile to collect all the published results and suggest their possible significance with particular reference to the results for clean surfaces.

Platinum.—The published data for platinum in various stages of outgassing are plotted in figure 1. This is essentially the same as the curve published originally by Richardson,[2] with the addition of recent data obtained by the writer. The writer's values and those of H. A. Wilson,[10] obtained in each case by observing a single specimen during outgassing, fall remarkably close to the same line. The other points which are more scattered represent individual values obtained by various observers under widely varying conditions. The approximation to the linear relation in

any case is probably within the limits of error. The point representing the value for clean platinum is indicated by the large crossed circle. It will be noted that the extreme values of A plotted differ by a factor of 10^7.

Tungsten.—The curve for tungsten in figure 2 is also similar to one published by Richardson, with the addition of more recent data by Dushman[4] and Kingdon.[17] The older data, obtained chiefly by Langmuir,[18] are for tungsten in the presence of various gases. In spite of the fact that A varies by a factor of 10^{12} the approximation to the linear relation is again very exact.

Thoriated Tungsten.—The data for a thoriated filament in various stages of activation are plotted in figure 3. The curve is taken directly

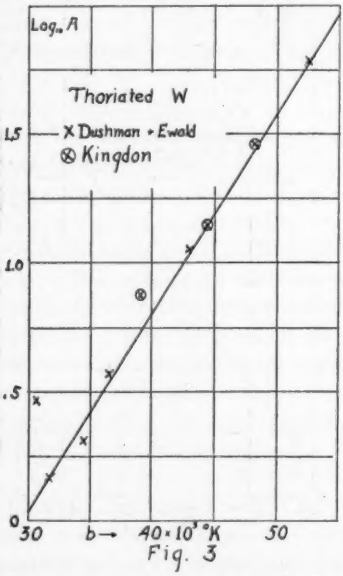

Fig. 3

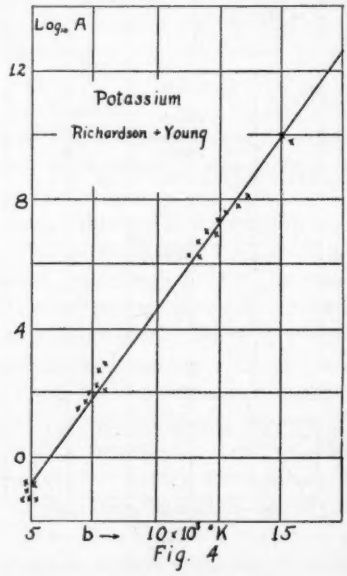

Fig. 4

from a paper by Dushman and Ewald,[19] with the addition of some earlier data by Kingdon.[17] Dushman states that his points satisfy the linear relation within the limits of error.

Potassium.—The curve for this metal in figure 4 is taken directly from a paper by Richardson and Young.[20]

Gold, Silver and Copper (Liquid).—Goetz[6] has recently obtained careful measurements of A and b for these metals through the melting points, extending his observations on the liquid surfaces up to the highest possible temperatures. Above the melting point b and A are found to increase rapidly with the temperature, due possibly to the effect of the vapor. His data have been plotted by the writer in figure 5 and it is interesting that

in this case also the linear relation is accurately satisfied. For liquid copper A varies over a factor of approximately 5×10^{13}.

For the sake of comparison all the curves have been plotted to the same scale in figure 6. These represent all the surfaces for which data on the concurrent variations of A and b have been published. In addition Richardson[2] has observed this linear relation for the positive ion emission from platinum. There is thus no known case where the relation fails to hold. In figure 6 the horizontal dotted line represents the value $\log A = 1.78$, $A = 60$, the theoretical value of Dushman's theory. It will be noted that all the curves, save for K, intersect on or near this line and that the only surfaces showing this value of A are those for which b happens to be about

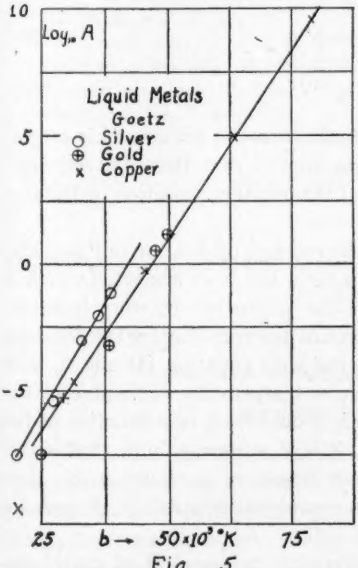

Fig. 5

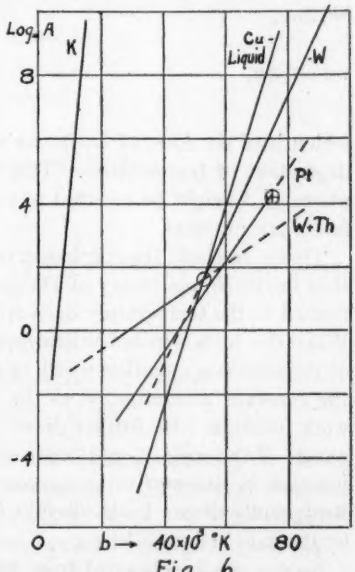

Fig. 6

52,000°K., corresponding to a work function of 4.5 volts. Surfaces showing a higher or lower value of b—*whether clean or contaminated*—show also correspondingly higher or lower values of A.

Evidently the curves of figure 6 may be represented by the simple empirical equation; (using now natural logarithms)

$$\ln A = \ln A_0 + \beta(b - b_0) \qquad (2)$$

where $A_0 = 60$, β, the slope, is a constant depending on the nature of the surface, and b_0 has the same value for all the more refractory metals. It would be of interest if β could be related directly to other physical properties of the surface, though it is difficult to see how this could be done.

However, for clean metals it is the value of the whole term $\beta(b - b_0)$ which is of interest since this term determines the observed value of A for the surface. Thus for metals for which $A = A_0$ this term must be zero, while for clean platinum it must be positive and for thoriated tungsten negative. If we set

$$\beta(b - b_0) = \alpha \tag{3}$$

and rewrite (2) in the form,

$$A = A_0 e^{\alpha}. \tag{4}$$

Then substituting this into (1) we have,

$$I = A_0 T^2 e^{-(b-\alpha T)/T} \tag{5}$$

Setting,

$$b - \alpha T = b' \tag{6}$$

we obtain,

$$I = A_0 T^2 e^{-b'/T} \tag{7}$$

which is of the form of Dushman's equation except that now b' is not independent of temperature. This means simply that the observed variations in A might be ascribed to a small temperature variation of the surface work function.

This is precisely the conclusion recently reached by Bridgman,[16] namely, that in the simple theory of Dushman a term has been neglected which is related to the temperature derivative of the (photoelectric) work function. When this term is included Bridgman obtains an expression for the constant of the emission equation which is identical with equation (4) above, with the constant α interpreted as the negative temperature derivative of the work function. He further shows that α should itself be a function of the nature of the surface, and hence of b. It is of interest to note that if this function be *assumed* to be approximately linear, as in equation (3), then Bridgman's theory leads directly to the empirical relation (2) demanded by the data in figures 1 to 6.

Now α can be obtained from measurements on the shift of the photoelectric threshold with temperature. Such shifts are known to be in general small, but Bridgman points out that they are large enough to account for the very large observed variations in A. Recent work in this laboratory by Dr. Warner, and some previous results of the writer[21] confirm this conclusion. Thus for tungsten Warner has found no appreciable shift in the photoelectric threshold up to 1100 deg. K. This means that $\alpha = 0$ and $A = A_0$, as it should for tungsten. On the other hand for platinum the writer has found $A = 14{,}000$ approximately, hence, $\alpha = 5.4$, while photoelectric measurements have shown a shift to the red in the threshold between 800° and 1200°C. which may have been as much as 50 A.U. This gives $\alpha = 4.5$ which is of the right sign and right order of magnitude.

* NATIONAL RESEARCH FELLOW.

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THE PHOTOELECTRIC LONG WAVE LIMIT OF POTASSIUM VAPOR

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Communicated September 4, 1928

Introduction.—In the investigation of the alkaline metallic vapors by light, two types of experiment have been performed. In one type[1,2] the vapor was used in equilibrium with the molten metal. In the other,[3,4,5] the vapor from the liquid metallic surface passed through a slightly superheated tube and then emerged from this tube into a vacuum, the vapor being illuminated and ionized after emergence.

In the first type of experiment, the observed long wave limit agrees within the limits of error with that predicted from the application of quantum ideas to the spectroscopic data, save that in the case of the work of Foote and Mohler with caesium, while a maximum of ionization was found at the proper wave-length, there was a gradual decrease in amount toward the longer wave-lengths. This ionization above the expected limit was accounted for on the basis of a cumulative process involving the energy of the electronic currents necessarily involved in their method.

In the second type of experiment, making use of potassium vapor issuing from a jet, a certain amount of discrepancy has occurred in the work of

different men. Williamson,[3] working with the total radiation from a mercury arc limited by filters, obtained a value between 2800 Å and 3000 Å, corresponding to the spectroscopic limit at 2856 Å. This was confirmed by Samuel.[4] Lawrence,[5] however, using a monochromator instead of filters, obtained no marked ionization for wave-lengths greater than 2610 Å, where a very sharp increase toward shorter wave-lengths was observed. This was attributed to a molecular form of the vapor, and indicated either that the molecular concentration was much greater than the atomic, or that the probability of molecular ionization was much greater than of atomic. The energy relations were such as to indicate ionization with dissociation. A rapid increase in the ionization current at about the same wave-length was present in Williamson's work. In pursuing the investigation, opportunity was found to repeat the previous work, using a monochromator instead of filters, and the results are now presented.

Apparatus and Method.—The apparatus was much the same as in the previous work, save for changes in dimensions, insertion of diaphragms to reduce condensation of vapor upon electrodes, etc. In the case of the curves shown in this paper, the source of light was a capillary, water-cooled quartz mercury arc, designed and made up by Mr. V. Vacquier of this department, who kindly loaned it to me, and assisted in making some of the observations. A Leiss monochromator was used instead of absorption screens. The light from the monochromator passed through a clear quartz plate set at 45° to the axis of the beam, so that part of the light was reflected to a potassium photoelectric cell for comparison purposes, and the rest entered the vacuum chamber through a system of diaphragms as in the previous work. The temperature of the liquid potassium was in most cases about 400°C., while the jet tube, 30 cm. in length with a diameter of 1 cm., was kept at a temperature of about 500°C. Simultaneous readings were made of the electron current from the photoelectric cell and of the positive ion current from the jet of vapor at wave-length intervals of 20 Å in most cases. Due to the fact that the rate of issue of potassium from the jet was not strictly constant throughout a run, and also to the fact that the lens focusing the slit image upon the jet of vapor and the window of the cell was not achromatic, the results are only qualitatively useful in considering the relative ionizing efficiency at different wave-lengths. However, different curves taken at different times agree in the main features.

Results.—The results are shown in figure 1, curves *a*, *b*, and *c*; *a* shows the positive ion current from the vapor, while *b* represents the electronic current from the photoelectric cell. Curve *c* was obtained by dividing the ordinates of *a* by the corresponding ordinates of *b*, thus giving an approximate indication of the relative ionizing efficiencies of the different wave-lengths of light.

First, we note that the ionization sets in sharply and definitely at the close group of lines near 3027 Å, while the much stronger set of lines near 3130 Å shows no comparable effect.

Second, there is a sharp increase in the ratio of the positive ion current to the photoelectric cell current for the line 2536 Å as compared with the line 2654 Å. This corresponds to the currents observed by Lawrence. The mercury lines between 2536 and 2654 were weak in comparison, hence, from these curves all that can be said is that a second type of ionization apparently sets in somewhere between 2536 and 2654. In the following discussion Lawrence's value of 2610 Å will be assumed for this limit. In most of the curves taken, the ratio rises to a maximum at about 2800 Å and then drops off again to a minimum at about 2600 Å. There it rises sharply to a maximum at about 2150 Å, and then drops off again down to 2050 Å. However, the intensities in this region are so low that the latter effect is uncertain.

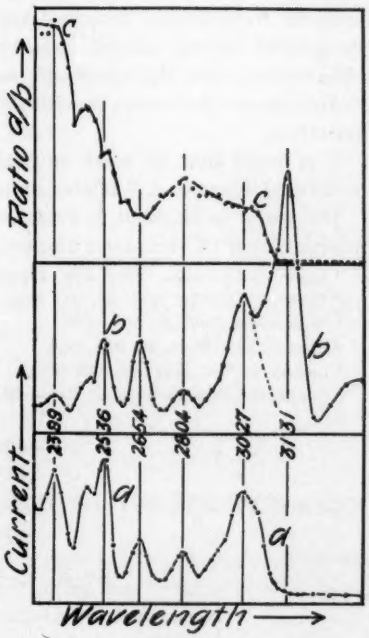

FIGURE 1

Discussion.—In considering the above, it is to be remembered that the spectroscopic limit for the potassium atom is 2856 Å, so that ionization is occurring in this case at least 170 Å above the expected limit. Since there seems to be no probability of a cumulative process occurring in this type of experiment comparable with that observed by Foote and Mohler, and since the results obtained at lower pressures by the other observers check well with the atomic limits, it seems very probable that the above data are to be accounted for on the basis of *molecular* ionization. In which case, there appear to be two types of ionization—one *without* dissociation, and one *with* dissociation.

Proceeding on this assumption, the ionizing potential of the molecule would be between 4.08 volts and 3.94 volts, corresponding to a limit between 3027 Å and 3131 Å for ionization without dissociation. From the 2610 Å limit we get 4.74 volts, corresponding to ionization with dissociation. From this the energy of dissociation of the *ionized molecule* is found

to be between 0.66 and 0.79 volt. From the limit for atomic ionization, 2856 Å, which corresponds to 4.32 volts, the dissociation potential of the neutral molecule is found to be 0.42 volt. This potential has been estimated by Carelli and Pringsheim[6] to have a most probable value of 0.61 volts, so that the result obtained above is apparently somewhat low. A correction of the 2610 Å limit for slit width would be in the right direction, but the amount is uncertain. We see from the above that the dissociation potential of the ionized molecule is apparently larger than that for the neutral molecule. If the band data for the ionized molecule were available, the dissociation potential might possibly be obtained from the convergence frequency of the oscillation levels, as was done by Carelli and Pringsheim for the neutral molecule. However, the writer can find no observations upon the spectra of the ionized molecule.

Any atomic ionization would seem to be obscured by the molecular ionization.

It is hoped that the work on potassium can be repeated either by the method of Kunz and Williams or by the method of Foote and Mohler.

The writer is indebted to Professor J. Franck for suggestions as to the interpretation of the above results.

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EMERGENT ENERGY OF PHOTOELECTRONS IN POTASSIUM VAPOR

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Communicated September 4, 1928

Introduction.—While the ionization of the alkaline metals by ultraviolet light has been definitely obtained, no results have been published which deal with the energy with which the photoelectrons emerge from the atoms or molecules of the vapor. The following results dealing with this subject are of a preliminary nature, and the values obtained are approximate only, owing to the limitations of the apparatus, and the difficulties of the method. An attempt was made to get information as to the direction of emergence as a function of the state of polarization of the light, but the polarizing prisms at hand were unsuited to the purpose.

In view of the results of the preceding paper, it seems probable that all the following phenomena are to be attributed to the ionization of molecules rather than of atoms. Two sets of observations are recorded, the first showing results obtained with the total radiation from a quartz mercury arc, while the second set was obtained making use of a monochromator with a quartz mercury arc.

Apparatus and Method.—In the results making use of the total radiation, a 110-volt Cooper-Hewitt quartz arc was run at about 90 volts. Spectrograms were made from the arc, both at high voltage, as used in the experiments, and also at low voltage. With high voltage, the mercury lines 2002 Å and 1973 Å came out quite strong, while 1941 Å was very weak, with 1850 not visible on the plates. At low voltage 2002 Å and 1973 Å were very faint; 1941 was strong, while 1850 Å was visible but faint. A low dispersion spectrograph was used, and no precautions were taken against absorption by the air. The vacuum chamber, jet, etc., were the same as used in the long wave limit work described in the previous paper. The light, after passing through the jet, emerged from the vacuum chamber and entered a potassium photoelectric cell for the purpose of checking the constancy of the source. The temperatures of the liquid potassium for the different runs varied from 300°C. to 450°C., the jet being superheated in all cases. A screen was used which could be placed in the path of the light before entering the jet chamber. This screen cut off wave-lengths shorter than 2940 Å. It is to be noted that this work in part was done when it was thought that the limit of the vapor was at 2856 Å, hence the use of the 2940 Å screen.

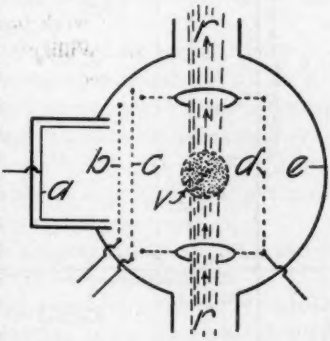

FIGURE 1

Owing to the relatively large wall emission due to the scattered light of wave-lengths greater than the long wave limit of the vapor, it was necessary to make use of a cage as shown at *d*, figure 1. The walls of the vacuum chamber were kept at a potential of about 3 volts positive relative to the cage, thus effectively reducing the area exposed to the scattered light. The efficacy of this scheme was shown in separate measurements of photoelectric currents from the walls, in which the wall currents when the grid *d* was connected to the walls *e* were about 300 times the currents obtained when the three-volt retarding potential was applied at *e*. The electrodes *b* and *c* were of fine nickel wires stretched vertically so as to drain off condensing potassium, and spaced about 3 mm. apart. The electrodes *b* and

c were separated by an interval of about 5 mm. As was later discovered, these dimensions were such as to give rise to difficulties with field penetration. But smaller spacing would soon have resulted in clogging as the potassium was condensing at a very rapid rate upon the interior of the chamber.

In taking data, the Faraday cylinder a was connected to a shunted Compton electrometer with a sensitivity of about 3000 mm. per volt. The grid b was kept at a constant potential of 8 volts negative relative to a. This served two purposes: i.e., preventing a from emitting photoelectrons due to scattered light, and preventing the positive ions from the ionized vapor from arriving at a until the negative ions had been completely stopped—as will be seen in the curves. The potential of c relative to b was varied, thus giving the retarding potential for the photoelectrons from the vapor. These potential differences, V_{bc}, are plotted as the abscissae of the curves. In one run (curves j, k, Fig. 2a) the potential of the cage d was kept at a constant negative value relative to the grid c, so that the photoelectrons from the vapor had 0.5 volt added to their emergent energy before they struck the retarding field.

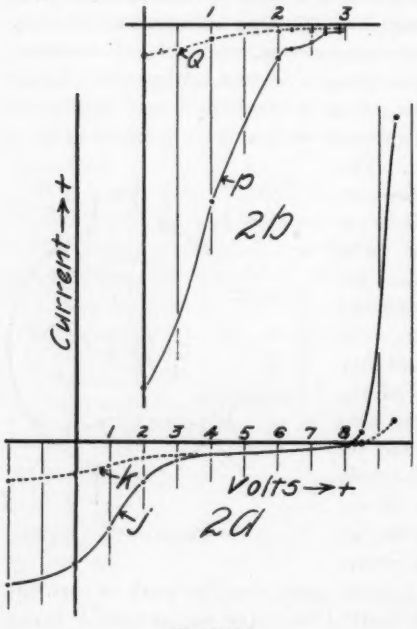

FIGURE 2

In the other run (p, q, Fig. 2b) there was no initial accelerating field, d being at the same potential as c. At each voltage, two readings were made, one using the full radiation from the arc, and one with the 2940 Å screen interposed.

In the results making use of monochromatized radiation, a Leiss monochromator was used together with the water-cooled capillary arc mentioned in the previous article. This arc gave a very high intensity immediately after starting with a fresh capillary, but, due to browning of the walls, the intensity dropped down to a much lower value after a short time. Because of this fact and also since the potassium had to be distilled very rapidly in order to get sufficient current, only two satisfactory curves

were obtained. In this case also, the photoelectric cell was used to check the constancy of the source during a run, the arrangement, however, being as described in the wave limit work. The cage *d* was not used in taking the data with the monochromatized radiation since it had become short-circuited to the walls *e* of the chamber in preceding observations. Fortunately, the use of the monochromator reduced the emission from the walls due to scattered light to such an amount that this did not constitute a serious difficulty.

Results.—Total radiation: In figure 2*a*, the curve *j* shows the current due to the total radiation as a function of the retarding potential V_{bc}, while *k* represents the current due to radiation passing through the 2940 Å filter. For these curves an accelerating potential of 0.5 volt was applied between *c* and *d*. In figure 2*b*, curves *p* and *q* show the corresponding currents when V_{cd} was zero: thus no initial acceleration was applied. Only such points were taken in the latter case as were necessary to determine the stopping potential.

Considering first the general features of the curves, we see that:

(1) The negative electronic current is reduced in magnitude by the retarding potential to a constant value, the voltage at which the constant value is reached being the applied stopping potential for the fastest electrons.

(2) At 8.5 volts the curve *j* bends sharply in a positive direction indicating the arrival of positive ions at the electrode *a*.

(3) There is a fairly definite inflection in the electronic curves *j* and *p* about 0.6 volt below the maximum applied stopping potential.

(4) That the introduction of the 2940 Å screen reduces the electronic current by from 80 to 90%, whereas observation at the same time showed that the current in the photoelectric cell was reduced by about 25%. Also separate tests showed that the currents due to scattered light upon the walls of the vacuum chamber were reduced in about the same ratio as those of the photoelectric cell.

(5) That curve *k*, figure 2*a*, shows a slight upward inflection at 8.5 volts, similar to *j*, so there still is some ionization at wave-lengths greater than 2940 Å.

The fact that the 2940 Å screen reduces the electronic current in the jet chamber to such a low value, while producing a relatively small reduction of the photoelectric cell current, is evidence that the currents measured are really due to electrons from the vapor and not from the surfaces exposed to scattered light.

The small amount of ionization observed even with the screen 2940 Å is in accordance with the newly established limit between 3027 Å and 3130 Å.

Considering the numerical relations to be expected, we shall confine our attention to curve *p*, figure 2*b*, since the features of this curve are more

sharply defined, though there is fair agreement between p, figure 2b, and j, figure 2a. First we note that the observed maximum applied stopping potential is 2.7 volts. This is not the effective stopping potential, however, because of the field penetration already mentioned. As will be shown later, the correction for this probably amounts to about 0.6 volt, to be subtracted from the observed value. Hence, the actual maximum stopping potential, or the emergent energy of the photoelectrons from the potassium molecules, is indicated to be 2.1 volts. If we assume the long wave limit of the vapor to lie between 3027 Å (4.08 volts) and 3131 Å (3.94 volts), we see that the radiation must have supplied an energy corresponding to from 6.18 volts to 6.04 volts to the electrons originally, requiring an incident wave-length of from 2000 Å to 2040 Å. This is in satisfactory

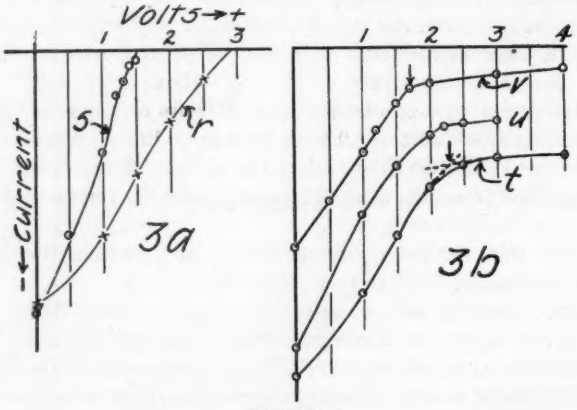

FIGURE 3

agreement with the fact that the hot arc was emitting the lines 2002 Å and 1973 Å with fairly high intensity, while 1941 was weak, with 1849 not present in the spectrograms.

Next, turning our attention to the inflection at the foot of the curve p, figure 2b, we note that it occurs about 0.6 volt below the stopping potential. Such an inflection could result from the presence of two groups of electrons, one of which had a lower emergent energy than the other. If the limits 2610 Å and 3027–3131 Å are the critical wave-lengths for ionization with dissociation and ionization without dissociation, respectively, the energy of dissociation of the ionized molecule corresponds to from 0.66 to 0.79 volt which checks fairly well with the 0.6 volt obtained from the inflection in the stopping potential curve, the indication being that the ionization wave limit is nearer 3027 Å than 3131 Å.

Monochromatic radiation: In curves r and s, figure 3a, are shown the currents for two wave-lengths 2399 Å and 3027 Å, respectively, plotted

to different scales. With zero retarding potential, shifting the monochromator from 3027 to 3131 Å, reduced the current to about $^1/_{12}$ that for 3027 Å. Part of this residual current may have been ionization due to overlapping of 3027 and part of it wall emission due to scattered light. An initial accelerating potential V_{cd} of one volt was applied in both curves.

In curve *s* we see that the applied stopping potential is about 1.5 volts. From this is to be subtracted the 1.0 volt initial accelerating potential. Consideration of the dimensions and spacing of the grids indicated the possibility of stray fields, so that the actual potentials of the wires do not represent the effective potentials of the regions between the wires. To get the amount of correction for this effect, it was necessary to reflect light into the vacuum chamber through the rear window so that a large enough emission could be obtained from the walls of the vessel for test purposes. Data were taken to plot three stopping potential curves, in which V_{ab} successively took the values -8.0, -1.0, -0.5 volt, as shown in curves *t*, *u* and *v*, respectively, of figure 3*b*. Here we see that the applied stopping potential decreases from about 2.3 volts to 1.7 volts as the potential V_{ab} is varied from -8.0 to -0.5 volt. From this we conclude that when the potential V_{ab} is -8.0 volts an applied stopping potential of 2.3 volts is equivalent to an effective stopping potential of 1.7 volts, or that a correction of about 0.6 volt must be subtracted from the observed stopping potential. This correction, then, taken together with that for the initial accelerating potential, gives 1.6 volts to be subtracted from the observed stopping potential in the curves *r* and *s*. In the case of curve *s*, for the wave-length 3027 Å, the resulting effective stopping potential is -0.1 volt, where it should be about zero for an ionization wave limit near 3027 Å. In curve *r*, we see that the observed stopping potential is 2.9 volts. Making the same correction as above, the effective stopping potential is 1.3 volts. Assuming that radiation of wave-length 2399 Å is capable of ionizing both with and without dissociation, and therefore calculating the maximum emergent energy from the 3027 Å limit, we get a value of 1.07 volts to be expected. Thus, there is a discrepancy of about 0.2 volt. In view of the approximate nature of the wave limits and the curve intercepts, the check may be considered as fairly satisfactory.

The evidence then seems to be strong that in these experiments the currents due to electrons emitted from the internal surfaces of the vessel have been made small relative to those due to the electrons resulting from photo-ionization of the vapor; and that the values of the stopping potentials thus obtained agree within the limits of error with those to be expected from the data relative to the ionization wave limits of the vapor.

By redesigning the apparatus, I hope to be able to improve the definition of the curves, and thus secure more accurate information concerning the process of photo-ionization of the vapor.

ELECTRIC CONDUCTIVITY AND OPTICAL ABSORPTION OF METALS

BY EDWIN H. HALL

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Communicated August 30, 1928

In a paper on "Electron Free Path and Supraconductivity in Metals," printed in the PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES for May, 1928, after calling attention to the fact that Sommerfeld's recently published "Electron Theory" requires "free paths" equal to some hundreds of times the "atomic distance," I suggested that we should regard the free path as terminated not in a collision of the electron with an atom but in its capture by a positive ion.

After this paper had been presented at a meeting of the National Academy of Sciences in April, 1928, Professor W. F. Durand of Stanford University called my attention to the fact that he had used the same conception of electron free path in a paper[1] printed many years before. I gladly make this acknowledgment, though I was entirely ignorant of the existence of Professor Durand's paper when I wrote my own. In fact, I rejoice to find occasional evidence that the views of electric conduction which I have been gradually evolving during the last fifteen years are not entirely singular and peculiar to myself.

Professor Durand's paper is an admirable discussion of free-electron conductivity and is well worth reading even now. It certainly contains the same general conception of free path that I have so recently proposed, though, as it does not emphasize this conception or dwell upon its advantages, it may well be that few readers of the paper have noticed that it departs from the ordinary theory of free-electron conduction in this particular.

In the paper referred to in my opening paragraph I have pointed out that a relatively small number of free electrons will be enough to account for the whole conductivity of metals, if free paths of several hundred "atomic distances" are supposed to prevail. A still smaller number will, of course, serve if, as I hold, the free electrons carry only a minor part of the current. Thus the specific-heat difficulty of which so much has been made, and which has done so much to discredit the natural view, originally held by every one, that the free electrons share the energy of the thermal agitation, may be abolished.

But it may be urged that the known optical properties of metals require us to suppose the existence within them of free electrons as numerous as, or even more numerous than, the atoms of the metals. The main purpose of the present paper is to examine the weight of this argument.

In the course of the discussion I shall make use of three alternative hypotheses concerning the mechanism of conduction:

Hypothesis A.—That the current is maintained entirely by free electrons sharing the energy of thermal agitation.

This was the hypothesis used by Lorentz in his "Theory of Electrons," published in 1909. In this book he says, on pp. 80 and 81, "It is well known that, in general, the optical properties of ponderable bodies cannot be deduced quantitatively with any degree of accuracy from the electrical properties. For example, though Maxwell's theoretical inference, published long ago in his treatise, that good conductors for electricity must be but little transparent for light, is corroborated by the fact that metals are very opaque, yet, if we compare the optical constants of a metal, one of which is its coefficient of absorption, with the formulae of the electromagnetic theory of light, taking for the conductivity the ordinary value that is found by measurements on electric currents, there is a very wide disagreement. This shows...that, in the case of the very rapid vibrations of light, circumstances come into play with which we are not concerned in our experiments on steady or slowly alternating electric currents. If this idea be right, we may hope to find a better agreement, if we examine the 'optical' properties as we may continue to call them, not for rays of light, but for infra-red rays of the largest wave-lengths that are known to exist. Now, in the case of the metals, this expectation has been verified in a splendid way by the measurements of the absorption that were made some years ago by Hagen and Rubens. These physicists have shown that rays whose wave-length is between 8 and 25 microns are absorbed to a degree that may be calculated with considerable accuracy from the known conductivity. We can conclude from this that, in order to obtain a theory of absorption in the case of these long waves, we have only to understand the nature of a common current of conduction."

Lorentz goes on, in Secs. 60 to 68, to show that, if we adopt the Drude-Lorentz theory of free-electron conductivity, make the free electrons as numerous as we please, and assume the time between collisions of a free electron with the atoms to be very small compared with the time of a light vibration, it is possible to account, by means of the free electrons, for Kirchhoff's law, Wien's law, and Planck's law in the form which it takes for long waves.

Lorentz does not evaluate definitely the number, n, of free electrons per unit volume needed for his purpose, but in Note 42 he calls attention to a discussion of this matter given by J. J. Thomson, at the end of Chapter 4 in his "Corpuscular Theory of Matter." On page 84 of this book we find the following passage, coming after a reference to the experiments of Hagen and Rubens:

"We can easily show that if k is the conductivity under steady forces,

then when the forces vary as sin nt the conductivity will be proportional to $k \frac{\sin^2 nT}{n^2 T^2}$, where $2T$ is the interval between two collisions [of a free electron with the atoms]. Thus, unless this interval be small compared with the period of the electric force the conductivity will be very materially reduced. Thus if T were as great as one quarter of the period of the force, so that $nT = \pi \div 2$, the conductivity would be reduced to $1 \div (\pi \div 2)^2$, or 0.4 of its steady value. As the diminution of the conductivity for light waves whose length is 4μ is less than this, we conclude that [$2T$] the interval between two collisions is less than one quarter [half] of the period of this light, or less than [$2\times$] 3.3×10^{-15} sec. Hence u the velocity [*net*, of the free-electron stream] under unit electric force, since it is equal to $\frac{1}{2} \frac{e}{m}$ [2] T, will be less than $\frac{1}{2}$ [omit?] $\times 3.3 \times 10^{-15} \frac{e}{m}$, and since k the conductivity is $n\ e\ u$, n [here the number of free electrons per cu. cm.] will be greater than [equal to] $k \div eu$, i.e., [greater] than [$\frac{1}{2}$]$\cdot \frac{k10^{15}m}{1.6e^2}$."

"For silver k is about 5×10^{-4}, and since $e \div m = 1.7$ [7] $\times 10^7$ and $e = [1.59 \times]10^{-20}$, we see that n for this metal must be greater than 1.8×10^{24} [5.5×10^{23}]."

Making the corrections indicated in [ ], I find $n = 5.5 \times 10^{23}$ approximately. The number of atoms in a cu. cm. of silver is about 6×10^{22}, so that, according to this calculation, the number of free electrons would be about 9 times as great as the number of atoms.[2,3] Such a ratio, with the free electrons sharing the energy of thermal agitation, is of course impossible. Accordingly, in spite of the admirable effort of Lorentz to account for the Hagen and Rubens observations by means of the Drude theory of free-electron conduction, it must, I think, be concluded that hypothesis *A* is unable to bear the burden proposed for it. We must either reject this hypothesis altogether or admit that the known facts of the optical behavior of metals tell us nothing definite concerning the mechanism of electric conduction.

Hypothesis B.—That the current is maintained entirely by free electrons which do not share the energy of thermal agitation.

This is the hypothesis toward which speculation in general on this subject appears to have inclined during recent years, against my protest. It is, for example, the hypothesis of Sommerfeld.

Sommerfeld has not, so far as I have seen, made any reference to the relation between electric conductivity and optical properties in metals. It seems to me, however, that the argument which I have quoted from Thomson depends not at all upon the underlying translatory energy of the free electrons. It does not assume that these electrons have or that they

lack the energy of thermal agitation. It would appear, then, that the numerical conclusion arrived at above, regarding the ratio of free-electron number to atom number, holds under hypothesis B as well as under hypothesis A. Is B, then, tenable?

Apparently not. The specific-heat difficulty may not, to be sure, present itself here in troublesome form, though Sommerfeld makes the energy of his free electrons depend, to some slight extent, on the temperature. But on other grounds the assumption that the free electrons are several times as numerous as the atoms seems inadmissible. For example, the "atoms" in such a case would not be atoms proper but the great majority of them would be multiply charged positive ions.

Hypothesis C.—That the electric current is maintained in part by free electrons sharing the energy of heat agitation, but mainly by an interchange of electrons in encounters between atoms and positive ions, the latter being, naturally, just as numerous as the free electrons. This is the dual theory of conduction which I have been advocating and illustrating for some years.

According to estimates, no doubt very fallible, which I published[4] in 1921, and which were based on a study of the electric conductivity, thermal conductivity and thermo-electric properties of many metals, the ratio of free-electron conductivity, k_f, to total conductivity, k, in these metals at 0°C. ranges from about 0.02 in iron to about 0.19 in bismuth. For copper, gold and silver it appears to be about 7%.

Let us consider the case of silver. At 0°C. its conductivity, k, is about 67×10^{-5} in absolute units, and so, according to my estimate, its value of k_f is about 4.7×10^{-5}. Taking the Drude formula for free-electron conductivity as

$$k_f = \frac{e^2 lnu}{4RT},$$

we thus find, for 0°C., $ln = 2.46 \times 10^{15}$. If now we take l, the mean "path" of the free electrons, as 200 times the "atomic distance," the latter being about 2.5×10^{-8} cm., we find n to be 5×10^{20}, which is somewhat less than 1% of the number of atoms per cu. cm. of silver. I have taken this particular length of electron path because it agrees very nearly with the value arrived at by Sommerfeld in the recent statement[5] of his conduction theory; but I might well have taken a still greater length. If we once admit that the free-electron path can be several times the atomic distance, there is no obvious reason why it may not be hundreds or thousands of times this distance, and the estimated value of n decreases in proportion as l increases. In taking such a value of l as to make the number of free-electrons only 1%[6] of the number of atoms, I have perhaps gone far enough to meet, or rather to avoid, the specific-heat difficulty.

The absorptive power of such long-path free electrons, for radiations of any ordinary wave-lengths, would doubtless be negligible. We must now consider what possibilities lie in the other mechanism of conduction, the direct passage of electrons from atoms to ions.

Let us suppose that a current of 1000 amperes is to be carried in the direction x along a silver bar of 1 sq. cm. cross-section. The mean "atomic distance" in silver is about 2.5×10^{-8} cm. and the mean projection of the atomic distance in the direction of x is about 1.5×10^{-8} cm. It is reasonable to suppose that the transfer of an electron from an atom to an adjacent ion is in some way connected with the heat oscillations of the atoms and ions. These oscillations are of course very irregular and have no definite single frequency, but the Debye theory of the specific heat of a solid, applied to the available data in the case of silver, gives for v_m, the "maximum frequency," a value about 4.5×10^{12} per second.

Let us now suppose that once in q vibrations of an ion the potential gradient which is maintaining the electric current determines the passage of an electron from an atom to an ion in the general direction of x, or inhibits such a passage in the opposite direction, one of these effects being as good as the other for maintaining a net current along x. If each electron passage covers the distance 1.5×10^{-8}, and if we suppose the number of ions, equally numerous with the free electrons, to be 1 for each 100 atoms, we get as the resultant current along x, per sq. cm. of cross-section,

$$I = 6 \times 10^{20} \times 1.5 \times 10^{-8} \times (4.5 \times 10^{12} \div q)\ 1.6 \times 10^{-20}.$$

If the current is to be 1000 amperes, I, in electromagnetic measure, will be 100, and so $q = 6500$, approximately. This does not seem to be an impossible or absurd value, though I recognize the fact that my picture of the transfer process leaves much to be desired.

It may be, indeed, that this particular matter should be looked at from a different point of view. It is possible that the ions should be regarded as not merely charged but polarized also, and therefore subject to a certain net orientation by action of the imposed electromotive force that maintains the current, an orientation which the thermal agitation of the atoms and ions would oppose. The effectiveness of the electromotive force for conduction may conceivably lie in this directive power, controlling to some slight extent the net direction in which the transits of the electrons, from atoms to ions, occur. Sir J. J. Thomson, as we shall presently see, imagined something not unlike this as a possible mode of conduction.

This second suggestion regarding the nature of associated-electron conductivity has the merit of indicating an explanation of the decrease of conductivity with rise of temperature. The first suggestion does not do this, but it is not necessarily to be rejected on that account. The passage of an electron out from an atom under such conditions that it will lodge

immediately in an adjacent ion, instead of going "free," is an operation which may be interfered with by the turbulence of thermal agitation.

The difficulty encountered at present in the attempt to form a satisfactory conception of associated-electron conductivity appears to be one of kinematics rather than of dynamics. It seems probable that wave-mechanics will have something to say in this connection. Perhaps it will be found permissible to suppose that the electron which unites with an ion may come as if *through* a chain of several atoms in one leap.

Let us next consider how the atom to atom mode of electron progression might be expected to function in the field of optical phenomena. It is helpful here to remember that more than twenty years ago J. J. Thomson, in close connection with the passage which I have quoted from his "Corpuscular Theory—and largely because of the weakness which that passage discovered in the free-electron theory of conduction—proposed an alternative theory. On pp. 49 and 50 he says, after briefly outlining the free-electron method of conduction, "It is easy to see, however, that a current could be carried through the metal by corpuscles which went straight out of one atom and lodged at their first impact in another; such corpuscles would not be free in the sense in which the word was previously used and would have no opportunities of getting into temperature equilibrium with their surroundings."

It may appear for the moment that I am about to lay the whole responsibility for the dual theory of conduction on the broad shoulders of the dean of British physicists, but I shall stop short of that. Thomson did not, so far as I know, make any attempt to combine the two suggested modes of conduction. Moreover, and this I regard as a distinction of great importance, he did not make the same use of the positive metal ions that I have made. In fact, having abandoned, for the time being at least, the idea of free electrons within the metal, he naturally does not think of positive ions as existing there. On the other hand, he conceives of "a large number of doublets, formed by the union of a positively electrified atom with a negatively electrified one," and proceeds to discuss the possible conductive working of such a mechanism, oriented by an imposed electromotive force, both for electricity and for heat. The theory of heat conduction to which he is thus led is exceedingly different from the one which I have since hit upon, but I need not dwell further on such differences. The fact of importance for my present inquiry is this, that Thomson worked out, for his second mode of electric conduction, a theory of connection between conductivity and optical absorption, which I am disposed to make use of for my own purposes, believing that my "associated-electron conduction" and his "second method" of conduction are enough alike to justify this proceeding. He begins his discussion as follows, on p. 89: "We have seen (p. 61) that Lorentz has shown that the long wave radiation can be

regarded as part of the electromagnetic pulses emitted when the moving corpuscles come into collision with the atoms of the substance through which they are moving, and he has given an expression for the amount of the energy calculated on this principle, which agrees well with that found by experiment. [It is to be remembered, however, that in the first quotation given above from Thomson the theory developed by Lorentz was found to require an improbably large number of free electrons.] But in the new theory, as in the old, we have the sudden starting and stopping of charged corpuscles and therefore the incessant production of electromagnetic pulses; these when resolved by the aid of Fourier's theorem [as Lorentz had resolved the pulses supposed to come from the accelerations of the free electrons] will be represented by a series of wave-lengths from zero to infinity. We must see if the energy in the long wave-length radiation at a given temperature would on the new theory be approximately equal to that on the old."

After several pages of mathematical discussion, in which, of course, certain arbitrary assumptions are made concerning the character and duration of the accelerations to which the conduction electrons are subject, in the two modes of conduction compared, Thomson gets, p. 97, for the first mode

$$W = \frac{2}{3}\frac{\alpha\theta\mu^2}{\pi^2 c^3} q^2 dq$$

and for the second mode

$$W = \frac{3}{4}\frac{\alpha\theta\mu^2}{\pi^2 c^3}\frac{b}{d} q^2 dq.$$

In each case W is the density of long-wave radiant energy, between the frequency limits q and $q + dq$, within the metal, $\alpha\theta$ is the kinetic energy per atom of the metal, μ is the refractive index, c is the velocity of light. In the second expression b is "the distance between the centers of the doublets" and d is "the distance between the charges in the doublet."

The author now remarks, "If, as we should expect in a good conductor, b is very nearly equal to d, the radiation on the new theory is to that on the old as 9 to 8. Thus the expressions are so nearly equal that in the present state of our knowledge [1907] we cannot say that in this respect the one theory agrees better with the facts than the other."

It is quite possible that Thomson would not today attach any great importance to the numerical similarity of the two expressions in question. So long as we are in doubt concerning the fundamental nature of radiation, we can hardly expect to have a completely satisfactory theory of the relation between metallic conduction and absorptive or emissive power of metals. The point which I wish to make here is merely this, that nothing

which we know concerning the optical properties of metals forbids us to hold a theory which presents as the chief mechanism of metallic conduction the passage of electrons from particles to adjacent particles of the metal without entering the "free" state or sharing the energy of thermal agitation. Such a mechanism Thomson has imagined for his "second method" and such a method is my conception of "associated-electron conductivity." So far as the evidence thus far produced in the present paper goes, hypothesis *C* appears preferable to hypothesis *A* and to hypothesis *B* in this particular, that it does not require an inordinate number of free electrons in order to account for the experimental observations of Hagen and Rubens concerning the relation between metallic conductivity and absorptive power for long waves of radiation.

But everything which I have quoted from Lorentz or from Thomson was written some twenty years or more ago, before the advent of Bohr. How much should the Bohr theory of radiation change the aspect of the question before us? This theory has thus far had to do, almost entirely, with atoms in the gaseous state, and with changes of condition occurring *within* the atom. If metallic conduction is carried on solely by free electrons, whether sharing or not sharing the energy of thermal radiation, and if the "collisions" of these free electrons with atoms are such as to result in no unions of electrons with the atoms, it is not obvious that the Bohr ideas will have any very important bearing on the relations of metallic conductivity and absorptive power. If, however, every free-electron "path" begins with the issue of an electron out from an atom, leaving it an ion, and ends with the union of the electron with an ion, forming thus an atom, and if every "associated-electron" passage takes an electron out from an atom into union with an adjacent ion, it seems highly probable that what has been learned during the past fifteen years about the internal structure and behavior of atoms will have much to do in clearing up the mystery which now surrounds the relations in question.

From this point of view the beginning of a "free path" within a metal is a process similar to photo-electric emission, accompanied or produced by the absorption of some definite quantum of radiant energy; and the termination of the free path, by reunion of the electron with an ion, is a reverse process accompanied by the emission of a definite quantum of radiant energy. Naturally, the quantum of energy needed to free an electron *within* the metal may be much less than the quantum required to free it *from* the metal. Probably, too, the quantum of energy needed to release an electron from an atom in the neighborhood of a positive ion, into union with which the electron is about to pass, is much less than the amount needed to release an electron into a free path.

It seems to me, however, that such considerations leave hypothesis *A* and hypothesis *B* still open to the objection which I, on the basis of my

first quotation from Thomson, have urged against them, that they require many more free electrons than there are atoms. On the other hand, hypothesis C, which puts the main burden of conduction on the associated-electron conductivity, appears still to be free from this objection.

The application of hypothesis C to the observations of Hagen and Rubens can be illustrated somewhat further as follows: An electron transit directly from an atom to an adjacent ion evidently can be effected in a much shorter time than that required for a "free path" covering several "atomic distances." Accordingly, associated-electron conductivity, k_a, will diminish less rapidly than free-electron conductivity, k_f, with increase of the frequency of electric-force alternations in radiation.

Thus, long-path free-electron conductivity may be regarded as negligible in the observations referred to. There is, however, no apparent reason why k_a should not continue nearly unimpaired under the radiation frequencies for which Hagen and Rubens found the Maxwell formula for absorption to hold, frequencies corresponding to wave-lengths between 8 and 25 microns, with vibration periods of 2.7×10^{-14} seconds and 8.3×10^{-14} seconds, respectively. But it may begin to fail with somewhat shorter wave-lengths. As I have already said, it seems probable that the k_a transits of electrons are conditioned in some way by the thermal vibrations of the atoms, the maximum frequency of which in silver is, according to Debye's theory of specific heat, about 4.5×10^{12}, with a vibration period of 2.2×10^{-13} second. If we assume the time occupied in an electron transit to be a hundredth part of this period, or 2.2×10^{-15} seconds, which is about 12 times the period of an 8-micron radiation-wave, we get a possible explanation of the fact that, according to Hagen and Rubens, the absorption of 8-micron radiation by metals agrees well with the formula of Maxwell (which uses the value of conductivity found with steady currents), while the rate of absorption of 1-micron radiation would not agree with this formula and would indicate a diminution of conductivity.

It should be remembered of course that radiant energy may be absorbed by means of operations occurring wholely within the atoms and having, therefore, nothing directly to do with the process of electric conduction. Lorentz plainly recognizes this fact in Sec. 120 of his "Theory of Electrons," written years before the Bohr theory of absorption and emission of energy, by means of changes of status within the atom, was formed. Accordingly, the suggestion which I have made[7] concerning supra-conductivity—that it may be due to very long free paths—does not imply that metals in the supra-conductive state should be incapable of absorbing radiant energy. But the optical qualities of metals in this state might be an interesting subject for experimental study. I should expect their absorptive power for long-wave radiation to be less than that of metals at ordinary temperatures.

[1] "The Interpretation of Electric Current Flow in Terms of the Electron Theory," *J. Elec., Power, Gas*, February, **1914.**

[2] O. W. Richardson, on pages 430–432 of his *Electron Theory of Matter*, refers to the work of Schuster, Jeans, and H. A. Wilson in dealing theoretically with free-electron conductivity under periodic forces. These authors derive a diminution formula which is different from the one used by Thomson. Schuster, applying his formula to the optical data accumulated by Drude, finds that "for all the commoner metals the number of free electrons in a given volume is from one to three times as great as the number of atoms present."

[3] Schuster, whose paper appeared in 1904, does not refer to the work of Hagen and Rubens and of course does not deal with the 4 micron wave-lengths of which Thomson makes so much. The difference between Thomson's estimate and Schuster's estimates of n does not materially affect the force of the argument I am making.

[4] *Proc. Nat. Acad. Sci.*, **7**, pp. 98–107.

[5] *Zeits. Physik*, **47**, February, 1928.

[6] Owing to the rate of increase of both n and the heat of ionization with rise of temperature, according to my theory, the number of free electrons here indicated might involve a contribution of about 3% to the specific heat of silver.

[7] See the paper referred to in my opening paragraph.

A DESCRIPTION OF THE ONTOGENETIC DEVELOPMENT OF RETINAL ACTION CURRENTS IN THE HOUSE MOUSE

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Communicated September 11, 1928

Several investigations upon the eyes of lower vertebrates (Chaffee and Adrian and their collaborators, and others) have given us much information as to the nature of the retinal response elicited by the action of light. These studies were made almost entirely employing excised eyes. Technical difficulties make it almost impossible to apply these methods to mammals. All such attempts employing eyes of the highest class of vertebrates have failed since the excised mammalian eye, tested immediately after removal, shows evidence of degeneration.

In a recent communication[1] (Keeler, Sutcliffe and Chaffee, 1928) it was shown that it is possible to obtain from normal intact unanaesthetized adult house mice, action-current responses quite similar to those found in the excised eyes of lower forms, while "rodless" house mice exhibited no changes in potential.

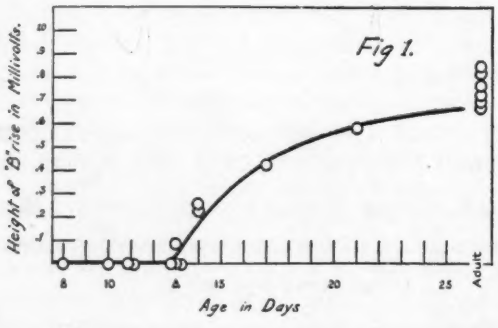
Apparatus.—The apparatus employed has been described by us, and in more detail[2] by Chaffee, Bovie and Hampson, 1923. The changes in potential are detected by a delicate Einthoven string galvanometer

in connection with a two-stage resistance-coupled amplifier and are recorded by means of sensitized paper upon a revolving drum.

Procedure and Results.—The trimodal curve of potential differences constituting the action-current record of vertebrate eyes, describes admittedly a very complex phenomenon, probably dependent upon several reactions localized in the retina and overlapping in time. The three modes are labeled "*A*," "*B*" and "*C*" upon the response curves of a 21-day-old mouse taken at an intensity of 538 meter candles, shown in figure 2.

The authors decided that a study of the beginnings of reaction in growing mice might shed some light in the direction of the proper interpretation of the nature of the reactions within vertebrate eyes, in general, since the times of onset of the supposed several reactions, if independent, might not arise simultaneously in ontogeny.

It has been shown (Keeler, 1927) that the rod is most probably the secretor of visual purple and that in normal mice these secretors (rods) are



entirely undifferentiated at birth. It was also pointed out that the internal nuclear and external nuclear layers separate about the fifth day after birth and that the rod buds do not grow out until the 7th or 8th day of postnatal development. If then, the action currents depend at least in part upon photochemical changes taking place in visual purple, we should not expect to find normal electrical responses in mouse eyes before the development of the rods, i.e., during the second week after birth. Thus the young mouse should be suitable material for studies into the ontogeny of the Retinal Action Currents.

To the end of determining the point in development of the mouse-eye at which the action currents are first discernible, a series of mice was examined from birth to maturity. In all animals which had not yet opened the eyes the lids were separated with forceps.

The height of the "*B*" rise was measured in millivolts in the cases where responses were detected. It will be seen from figure 1 that the youngest

mouse to exhibit action currents was 13 days old, while 3 others of the same age gave no response. The height of response increases with age, although it has not reached the adult height even in mice 21 days old.

In order to study more precisely this development, numerous records were taken for the same animal at intensities of light between 0.09 and

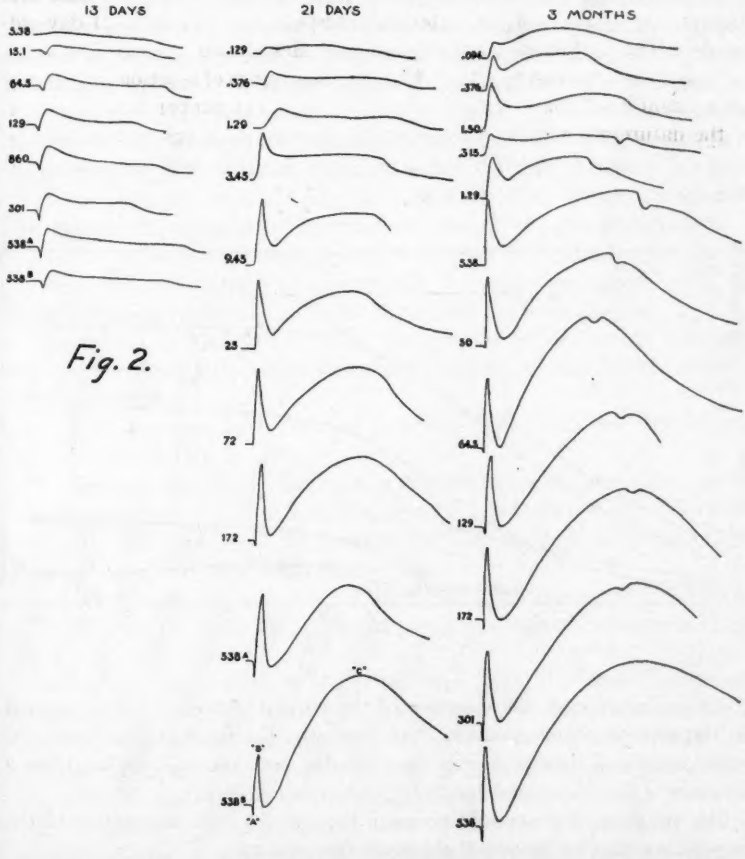


Fig. 2.

540 meter candles. The total increase of intensity for this range is about 6000-fold.

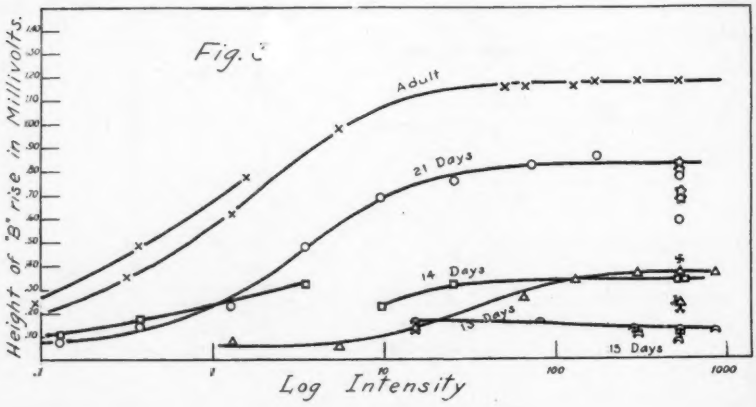
In figure 2 are shown tracings for an intensity series using short time exposures upon animals of 13 days of age, 21 days of age, and adult. The numbers preceding each curve denote the intensity of light employed for stimulation in each case.

It will be noticed at once that the curves obtained for the 13-day-old

mouse differ greatly in form from those of the older animals, yet in all three they increase in height with increase in intensity. In the 13-day-old animal, however, there is present a negative "*A*" deflection comparable to the "*A*" found in older animals only at the highest intensities. There is no appreciable "*C*" rise in the curves of the youngest animals.

In the 21-day-old animals the "*C*" rise becomes very prominent although not nearly so great as in the adult mouse. The valley ordinarily made in the "*C*" curve by the turning-off of the light is quite noticeable in the records for adult mice. This is commonly referred to as the "off effect."

At all ages the height of the "*B*" rise, the depth of the "*A*" deflection, and the height of the "*C*" (when present), increase with increase in intensity.



An explanation of the meaning of the various curves is not attempted in the present communication. As, however, the most obvious and constant feature of these curves is the "*B*" rise, we have used its height as a measure of the response as has been done in earlier papers.

For the present we can do no more than give a bare description of the results, hoping that these will aid in a future analysis.

In figure 3 are charted several intensity series taken upon animals of ages varying from 13 days old to adult. The record for the eye of the animal at 15 days of age is probably that of a defective eye, whereas the other records are considered those of normal-eyed mice.

The records were taken in order from low to high intensities with intervals of darkness of from 3 to 5 minutes between exposures. After the taking of the first series in the case of the 13-day-old mouse and the adult,

a second series of extremely low intensities was obtained. These curves are of the same general form as those obtained from lower animals such as the frog and lizard.

The effect of adaptation or supersensitization is seen in the curves for the 13-day-old, 21-day-old and adult. That is to say, when an eye has once been tested and then allowed to remain in the dark for a long time, if another record then be made at the same intensity the latter response will be larger than the former. For example, the stars in figure 3 represent the height of "*B*" rise at the highest intensity for adult mice without adaptation. The cross mark above represents the increased response after a certain amount of dark adaptation acquired during the time of running through the series of nine tests shown by cross marks.

If one plots for older animals, the logarithm of the height of the "*B*" rise against the logarithm of the intensity, a sigmoid curve is suggested.

It is hoped to make a more extensive study of the action currents in the mouse, employing curare to anaesthetize the motor end plates with the hope of separating the adaptational effect from the basic reaction.

Summary and Conclusions.—The ontogeny of action-current responses has been studied in the intact unanaesthetized house mouse, obtaining the following results:

1. The age at which the first potential differences are visible was found to be the 13th or 14th day.

2. In young mice the reaction is quite different from that found in the adult, consisting of a deep, wide, negative "*A*" deflection followed by a low wide "*B*" rise. The "*C*" rise is not found even in the records taken with stimulation of 538 meter candles intensity.

3. As the animal grows, the reaction gradually takes on the adult form, although even at 21 days of age it is obviously inferior in size to that of the adult.

4. In mice from 21 days of age on, there is no "*A*" deflection at the lower intensities, but at the highest intensities it is present, increasing in size with the increase in intensity. This increase in size of the "*A*" deflection with increase in intensity is found also in the youngest animals where the "*A*" rise is present at all intensities.

5. The effect of adaptation is seen in these records, in that an eye stimulated after short and long exposures to darkness differ greatly in size, the more adapted giving the greater response.

6. If the height of the "*B*" rise of any age be plotted against the logarithm of the intensity the result is a sigmoid curve.

7. Adapted eyes show a smaller "*C*" rise than unadapted eyes.

[1] Keeler, Sutcliffe and Chaffee, 1928, *Proc. Nat. Acad. Sci.*, **14**, No. 6, pp. 477–484, June, 1928.

[2] Chaffee, Bovie and Hampson, 1923, *J. Opt. Soc. Amer.*, **7**, No. 1.

A FIFTH ALLELOMORPH IN THE AGOUTI SERIES OF THE HOUSE MOUSE

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Communicated September 10, 1928

Experiments with a strain of black-and-tan mice obtained from an English fancier* have shown that these mice contain a hitherto undescribed gene which is allelomorphic to yellow, agouti, and non-agouti (black), and consequently forms a fifth member of this series of multiple allelomorphs.

The black-and-tans used are jet black dorsally with a bright yellow belly and retain this coloration throughout life. They breed true and produce large litters averaging about 7.5 young per litter. When crossed with black mice they produce only black-and-tans indistinguishable from the pure type. Such F_1 animals mated *inter se* produce only black-and-tans and blacks in a monohybrid ratio (actual numbers 80:31). Crossed with agouti (wild type) they produce only agoutis with yellow bellies. The cross of black-and-tan with yellow (heterozygous for agouti) yields two types of young in about equal numbers; viz., yellows or sables (dark yellows and yellow-bellied agoutis (actual numbers 19:22). The F_1 yellows or sables crossed with black produce equal numbers of yellows (or sables) and black-and-tans (67 of each in the experiments to date) showing that the F_1 sable or yellow type is heterozygous only for yellow and black-and-tan, and that yellow and black-and-tan are allelomorphs. The F_1 yellow-bellied agoutis when crossed with black produce only black-and-tans and gray-bellied agoutis (ratio 74:95) showing that black-and-tan and agouti are allelomorphs. The cross of black-and-tan with white-bellied agouti (a dominant allelomorph of the wild type) produces agoutis with bellies intermediate between yellow and white.

These results indicate that the gene for black-and-tan is allelomorphic to yellow, agouti, white-bellied agouti and non-agouti. It is completely dominant to non-agouti, the lowest member of the series; in its effect on the dorsal pigmentation it is recessive to wild type, white-bellied agouti and yellow, so that from this standpoint the order of dominance in this series may be written as follows:

A^Y—yellow
A^W—white-bellied agouti
A—wild type agouti
a^T—black-and-tan
a—non-agouti (black or brown)

It is interesting that the similar black-and-tan variation in the rabbit is also an allelomorph of agouti and non-agouti and occupies a similar position in the series (Castle and Fish, 1915), the only difference being that wild-type agouti in the rabbit has a white belly and so is equivalent to the A^W member of the mouse series.

The appearance of five allelomorphs provides an opportunity for the study of the phenotypic effects of mutations at the same locus. In the agouti series these effects are more varied than in some other series. The chief effect seems to be on the relative proportions of black and yellow pigments as observed by Wright (1917) and the physiological effects of this series of genes on coat color may be assigned as Wright showed to his group $2a_1$. In passing from the highest to the lowest member of the series there is a progressive increase in the apparent quantity of black pigment, the yellow mutant showing least and black most. The steps in this progression are not equal, only those between yellow and agouti and between agouti and black-and-tan being well marked. The effect on yellow pigment is apparently non-linear in the series as constituted at present since reduction of yellow to white appears only in the second member of the series, viz., white-bellied agouti, whereas yellow of full intensity appears again on the belly of black-and-tan, the fourth member. The greatest discontinuity in the series appears between yellow and white-bellied agouti, for here at one step the black pigment which masks the yellow over most of the fur in the wild type is greatly reduced while the belly is changed from cream or white to yellow. It is noteworthy, too, that only the yellow mutant at the top of the series acts as a lethal and alone shows the tendency toward the early accumulation of fat. (Danforth and deAberle, 1927.) Yellow on the whole is the most peculiar member of the series and in these several ways is most unlike the other allelomorphs.

The contrast between the pigmentation of the back and belly which is most marked in the agouti types and in black-and-tan, but which occurs also in black and brown, probably does not imply a differential effect of these allelomorphs on the dorsal and ventral pigmentation, but is more probably due to a regional differentiation of the tissues of back and belly whereby one surface reacts more strongly than the other to general pigment-forming agencies. A similar contrast is apparent in white spotted mice in which the back usually develops more pigment than the belly. Since the back and belly show differences in the rate of development of both fur and pigment this may well be the clue to the physiological interpretation. Such non-homogeneity of the tissues (sensu Iljin, 1928) at a critical time may account for regional differences in effects, while graded variations in the speed or time of production of general pigment reagents, each grade corresponding to a member of this series of genes, may account for the graded series of general effects on black and yellow pigment. There

is at present but little direct evidence to support this general assumption and it is possible that physiological reactions (due to other genes), which occur subsequently to those guided by the agouti genes may be of considerable significance, as suggested by Wright's (1925) study of the albino allelomorphs in the guinea pig.

Finally, it must be pointed out that although the black-and-tan variation in the mice studied in these experiments apparently arose through a mutation at the agouti locus, the same pattern has arisen in at least one other way, showing that the genes at the agouti locus are not the only ones which affect the relative proportions of black and yellow pigments. Previous experiments with another strain of black-and-tan mice (Dunn, 1916 and 1920), also obtained from English fanciers, showed that in those mice black-and-tan was due to the accumulation of multiple genes for the increase of black pigment in mice that were genetically yellows. Since this type is genetically different from the black-and-tans used in the present experiments (although phenotypically similar or identical) the first type will be referred to as "black-backed yellows" and black-and-tan will be reserved for the allelomorph of agouti which corresponds to the black-and-tan of rabbits. The black-backed yellows did not breed true, gave the small litters characteristic of yellow varieties, and when crossed with the wild type produced typical yellow mice in the second generation, showing that a gene for yellow had been introduced by the black-backed yellow. It was shown also that the same multiple genes which convert a yellow into a black-backed yellow may be transferred to an agouti and convert it into a black mouse with a gray belly. It appeared that the same sort of darkening genes are responsible for the continuous series of yellow types extending from yellow through sooties and sables to black-backed yellows, the shade probably depending on the concentration of darkening genes. The same genes were probably involved also in the present experiments since sooties, sables and dark agoutis appeared after crossing black-and-tan with yellow. The F_1 sables from this cross do not owe their darkness to the black-and-tan gene, since similar sables appeared also from the cross of F_1 sable by black and these were shown not to carry black-and-tan. Sables have also been produced by crossing yellows with intense blacks and in this cross the black-and-tan gene is not involved. It appears therefore that the black-and-tans used had not only the black-and-tan gene but also multiple genes tending to intensify and increase black pigment. Thus it happens that yellow and black-and-tan appear to form intermediates when crossed, although it is probable that this is not due to interaction of these two allelomorphs but to other genes.

* Mr. W. Bell of Norwich. It is a pleasure to acknowledge here the kindness of Mr. J. N. Pickard and Mr. Stewart Russell of the Animal Breeding Research Department of the University of Edinburgh, who obtained these mice for me.

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DETERMINATION OF ALL THE GROUPS WHICH CONTAIN A GIVEN GROUP AS AN INVARIANT SUBGROUP OF PRIME INDEX

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Communicated September 12, 1928

Since every solvable group contains an invariant subgroup of prime index a method for constructing all the possible groups which contain a given group as an invariant subgroup of prime index includes the construction of all the possible solvable groups. Let H represent the given group of order h and let G represent a group of order $g = ph$, p being a prime number which contains H invariantly. When G is represented as a regular substitution group H will be represented as an intransitive group which is a simple isomorphism between p regular groups. To find all the possible groups G it is therefore only necessary to find all the possible sets of substitutions which can be added to the given intransitive substitution group H so as to obtain distinct regular groups of order ph.

Let t_1 be a substitution which with H generates a regular group G. The p transitive constituents of H must be transformed cyclically by t_1. Let t be a substitution which is commutative with every substitution of H and transforms these transitive constituents cyclically in the same manner as t_1. It, therefore, results that t_1t^{-1} is a substitution which transforms into itself every one of these transitive constituents. It is therefore the product of p substitutions $s'_1, s'_2, \ldots, s'_p$ on the letters of these p transitive constituents, respectively. These substitutions must transform H into itself and must transform the transitive constituents of H to which they relate according to the same operator in their group of isomorphisms. Let each of the substitutions $s_1, s_2, \ldots, s_p$ represent this operator written on the respective letters of the transitive constituents of H in such a way that the substitution $s_1s_2, \ldots, s_p$ is commutative with t. It is obvious that the substitution $t_1 = s'_1s'_2, \ldots, s'_pt$ can be transformed by means of substitutions in the conjoints of the transitive constituents of H into $s_0s_1s_2, \ldots, s_pt$, where s_0 is found in the conjoint of s'_1.

As a first result of this method we have the following theorem: *The number of distinct groups which contain a given group as an invariant subgroup of a given prime index and transform its operators according to the same operator, or according to the same set of operators, in its group of isomorphisms cannot exceed the order of this group.* In the special case when $h = p = 2$ the number of these groups is obviously equal to this order. When $(s_1 s_2, \ldots, s_p)^p$ is an operator of H then s_0 must be found in the first transitive constituent of H. This is obviously always the case when H is abelian. Moreover, s_0 must always be commutative with s_1 since $(s_0 s_1 s_2, \ldots, s_p t)^p$ is a substitution of H and t is commutative with all the substitutions of H. When H is abelian then the order of s_0 may be supposed to be a power of p, and s_0 is not the p^{th} power of a substitution which is commutative with s_1 and appears in the first transitive constituent of H. All the powers of s_0 which are prime to its order give rise to the same group whenever H is abelian, since the operators of the group of isomorphisms which transform every operator of H into the same power of itself are invariant under this group of isomorphisms. From these theorems it follows directly that the cyclic group of order 4 cannot appear in more than four groups of order 8, and it actually appears in four such groups. It also results therefrom that the cyclic group of order 6 appears in exactly three groups of order 18.

The preceding considerations furnish a proof of the following theorem: *If a group H of order h involves no invariant operator besides the identity but admits an automorphism of order p, p being a prime number, then there is one and only one group of order ph which involves H invariantly and transforms it according to the given automorphism.* It should be noted that this theorem is independent of whether the given automorphism of order p is an outer or an inner automorphism. When it is an inner automorphism the group in question is the direct product of H and a group of order p. As an illustration of this theorem it may be noted that the alternating group of degree greater than three and not of degree six appears in just two groups of twice its own order. As a matter of fact this is also true of the alternating group of degree three but this case comes under other theorems noted above. The alternating group of degree six appears in four groups of order 720.

In the construction of the possible groups G it is obviously only necessary to consider one inner isomorphism of H, and it is usually most convenient to select for this one the identity isomorphism. The number of outer isomorphisms that require consideration does not exceed the number of the sets of conjugate subgroups of order p in the quotient group of the group of isomorphisms of H with respect to its group of inner isomorphisms. In the case of a complete group it is therefore unnecessary to consider any isomorphism besides the identity isomorphism. While the only outer

isomorphisms which require consideration are those which correspond to subgroups of order p in the given quotient group it should not be assumed that a group necessarily corresponds to such an outer isomorphism.

A very elementary illustration of a case where there is no such group is furnished by the dihedral group of order 2^α, $\alpha>3$. The group of inner isomorphisms of this H is the dihedral group of order $2^{\alpha-1}$, and there are three operators of order 2 in the quotient group of the group of isomorphisms of H with respect to its group of inner isomorphisms. At least one G corresponds to each of two of these operators of order 2 but no G corresponds to the third operator of order 2 when this is so selected that the corresponding operators in the group of isomorphisms transform the operators of highest order in H either into their $2^{\alpha-1}-1$ power or into their $2^{\alpha-1}+1$ power, and the non-invariant operators of order 2 in H into themselves multiplied by an operator of highest order in H. The square of such an operator has therefore to transform H in the same way as one of its operators of highest order. This square could not be this operator of highest order since the corresponding isomorphism of order $2^{\alpha-1}$ does not make this operator correspond to itself.

It is now easy to determine all the groups of order $2^{\alpha+1}$ which contain the dihedral group H of order 2^α, $\alpha>3$. It results directly from what precedes that there are two such groups which transform H according to an operator in its group of inner isomorphisms and that there are two additional groups which involve operators of order 2^α. One of these two groups is the dihedral group of order $2^{\alpha+1}$. There is one group in which the operators of highest order in H are transformed either into their $2^{\alpha-1}-1$ or into their $2^{\alpha-1}+1$ powers. Hence, *there are exactly five groups of order* $2^{\alpha+1}$ *which contain the dihedral group of order* 2^α, $\alpha>3$. One of these groups involves four dihedral groups of order 2^α. Each of two others involves two such dihedral groups, while each of the remaining two involves only one such group. Each of four of these groups contains also an abelian subgroup of index 2 but the fifth does not have this property.

If the order of a dihedral group H is $2p^m$, p being an odd prime number, then H appears in only one group of order $4p^m$, whenever $p-1$ is not divisible by 4. This is the direct product of H and a group of order 2. When $p-1$ is divisible by 4 then H appears in an additional group of order $4p^m$. This second group involves only operators of order 4 in addition to the operators of H. Hence there results the following theorem: *If the order of a dihedral group is twice an odd number this dihedral group is a subgroup of index 2 of exactly* $2^k+2^{l-1}-1=k_1$ *groups, k being the number of distinct odd prime numbers of the form* $4n+1$ *which divide the order of this dihedral group and l being the number of distinct prime factors of its order.*

By means of this theorem it is easy to find the number of groups which contain any other dihedral group as a subgroup of index 2. It is only

necessary to multiply the given number by the number of groups which contain one of the dihedral Sylow subgroups of order 2^m contained in the given dihedral group as a subgroup of index 2. Hence, it results that a dihedral[1] group whose order is divisible by 16 or by no higher power of 2 than 8, 4 or 2 appears as a subgroup of index 2 in $5k_1$, $4k_1$, $3k_1$ or $2k_1$ groups, respectively. In a similar manner it may be proved that if the order of a cyclic group is divisible by 8 and by 1 different odd prime numbers it is found as a subgroup of index 2 in 6.2^1 groups. If its order is not divisible by 8 it is found as a subgroup of index 2 in 2^1 times the number of groups in which its Sylow subgroup of order 2^m appears as a subgroup of index 2; i.e., in 4.2^1, 2.2^1 or 2^1 distinct groups as 4, 2 or 1, respectively, is the highest power of 2 which divides its order.

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COLOR CHANGES IN EXCISED PIECES OF THE INTEGUMENT OF ANOLIS EQUESTRIS UNDER THE INFLUENCE OF LIGHT

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Communicated September 11, 1928

While at the Harvard Biological Station, Soledad, Cuba, during July and August, 1928, I investigated color changes in several species of Cuban lizards. In addition to experiments dealing with color changes in intact animals, observations were made of the effect of various light intensities upon excised portions of integument.

Although most of the common species of Anolis show color changes in the intact animals, only in the case of *Anolis equestris* were positive results obtained in experiments involving excised skin. *Anolis equestris* has a color range from very dark brown to bright green. The unoperated animal, left undisturbed but confined to a cage in a diffusely lighted laboratory, usually remains bright green throughout the day. If, however, the animal is exposed to bright sunlight, its skin at first becomes dark brown and then turns green again. It is probable that *A. equestris* reacts to assume the brown state under intense illumination and then responds to the high temperature of continued exposure to direct sunlight by again becoming green. Apparently diffuse daylight is of too low intensity to cause melanophore expansion. In the absence of light these animals are persistently green. Alternate exposure of intact animals to direct sunlight and then to diffuse daylight showed that color changes usually require many minutes and sometimes several hours.

Anolis equestris exhibits two peculiarities as regards color change. The first of these consists of its reaction to excitement. As stated above, *A. equestris* is ordinarily green in diffuse daylight. But if one enters the room where one of these lizards is confined the mere presence of a human being near the cage serves as sufficient stimulus to induce a change from green to brown. The brown color thus induced persists as long as one remains in sight of the animal, following which the green state is once more assumed. If the animal is removed from the cage while in the brown state and is held so as to cause it to struggle the color of the skin becomes bright green. Apparently, mild excitement causes melanophore expansion while a higher degree of excitement brings about melanophore contraction. Without further experimentation one can only surmise the nature of the mechanism which controls this dual response of skin melanophores to excitement. The reaction is, however, suggestive of one of two possibilities: either secretion of pituitrin under mild excitement followed by secretion of adrenalin under greater excitement, or expansion of melanophores following a response of the nervous system to mild excitement and this expansion followed by contraction which is induced by adrenalin secreted only under higher excitation.

A second peculiarity seen in the color changes of *A. equestris* is its reaction to a focused beam of sunlight. The green color induced by handling an animal persists as long as it is held in restraint but if a hand lens be so held that it focuses a beam of bright sunlight on a small area of dorsal skin of the animal for one minute the skin area thus illuminated turns slowly brown. This local expansion of melanophores is quickly followed by contraction and by the reappearance of the green condition when the lens is removed. Since the area exposed to the concentrated beam of light must be subject to a high temperature which ordinarily causes melanophore contraction, the local expansion of melanophores in this case is difficult to explain. The discovery of local response of melanophores to stimulus did, however, suggest the experiments on excised skin patches which are the subject of this paper.

In testing the reaction of excised pieces of integument to light, patches of dorsal skin were removed, transferred to watch glasses containing physiological salt solution, and exposures made to different intensities of light. Allowing one half hour for recovery from the shock of operation, skin patches were first exposed to diffuse daylight for an additional half hour. The green state which appeared immediately after operation persisted as long as the material remained in the laboratory. This condition is quite in accordance with results obtained with the intact animal. The watch glasses were then transferred to direct sunlight. Here the excised skin became dark brown in *40 seconds*. The watch glass was then moved to nearby shade where the skin again became green after *15 seconds*. Re-

peated trials showed that the change from green to brown required 30 to 40 seconds and the reverse change, from brown to green required 12 to 15 seconds. In these experiments the temperature in direct sunlight varied from 32°C. to 36°C., while that of the nearby shade ranged from 31°C. to 33°C. When trials were repeated every half hour after operation, skin patches continued to respond for three hours, after which color changes failed. Artificial light occasioned similar responses in excised skin but at a much slower rate.

To test the degree of localization of the effect of light upon excised skin, patches of integument were used which were about two inches long and half as wide. A watch glass containing such a strip was so placed that one half of the strip was exposed to direct sunlight while the other half was in the shade. Under these conditions, the lighted half of the strip turned dark brown and the shaded half remained bright green. Within one minute after a reversal of light conditions the colors of the two halves had also reversed themselves.

These experiments indicate that the melanophores of the integument of *Anolis equestris* are capable of responses to light when isolated from the action of hormones and when separated from the nervous system as a whole. These color changes in excised skin patches may depend on impulses received through end organs still intact after operation or they may occur as a result of the direct effect of light upon the melanophores.